Title

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Publication Date

1970-05-01

Thesis/dissertation

UCRL-19157

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(Ph.D. Thesis)

May 1970

AEC Contract No. W-7405-eng-48

LAWRENCE RADIATION LABORATORY
UNIVERSITY of CALIFORNIA BERKELEY

UCRL-19157

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THE ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF α-$NiSO_4 \cdot 6H_2O$ AT LIQUID HELIUM TEMPERATURE

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ABSTRACT

The electron paramagnetic resonance (EPR) spectrum of α $NiSO_4 \cdot 6H_2O$ has been studied at temperatures ranging from 1.2 to 4.2°K. The EPR spectrum of the powder is dominated by an intense absorption near 10kG at 9 GHz. For single crystal measurements this is shown to be an allowed transition between the Ni^{2+} spin states when the magnetic field is perpendicular to the unique axis of the spin Hamiltonian. Ananlysis gives $E = 0.035 \pm 0.005$ cm^{-1}, if we assume that $D = 4.74$ cm^{-1} as found by Fisher et al. from thermodynamic measurements.

The far infrared spectrum from 3 cm^{-1} to 25 cm^{-1} has been observed with magnetic fields up to 50 kG along the c-axis both at 1.3 and 4.2°K. The zero field spectrum at 1.3°K is discussed in terms of a nearest neighbor exchange interaction model. The value of $J = 0.12$ cm^{-1} is obtained for the Ni^{2+} exchange interaction between unlike neighbors. The exchange interaction between like Ni^{2+} is discussed in terms of excitons and the D value of Fischer et al.

The EPR spectra at X-band and K band of impurity ions Co^{2+}, Mn^{2+}, and Cu^{2+} have been observed. The spin Hamiltonian parameters necessary to describe the angular dependence of the Co^{2+} spectra are $g_{\parallel} = 6.\overline{44}4$, $g_{\perp} = 3.162$, and $A_{\parallel} = 30 \times 10^{-4}$ cm^{-1}. The magnetic z axis of the Co^{2+} ions forms the angle $\Phi = 60.7°$ with respect to the c axis of the crystal lattice. These parameters do not yield an exact description

of the experimental data. The exchange interaction between the Co^{2+} and Ni^{2+} ions is discussed. The g values for Cu^{2+} are $g_{\|} = 2.890$, $g_{\perp} = 2.481$. For Cu^{2+} the angle is found to be $61.8°$. The effect of exchange on the Cu^{2+} g values is discussed. The Mn^{2+} spectrum was found to be exceedingly complex and could not be described by the usual spin Hamiltonian parameters. This had been attributed to the strong exchange interaction.

The magnetic properties of $NiSo_4 \cdot 6H_2O$ have also been discussed with regard to the more detailed description of the spin Hamiltonian parameters of the Ni^{2+} ions and the size of the exchange interaction made possible by spectroscopic techniques. The crystal structure of α-$NiSO_4 \cdot 6H_2O$ is described in detail.

I. INTRODUCTION

A great deal of electron paramagnetic resonance (EPR) work has been dedicated to the study of paramagnetic impurities in diamagnetic lattices.[6] These studies have yielded a large amount of information about the magnetic parameters of the transition metal ions. By growing single crystals with sufficiently small amounts of paramagnetic impurities, any perturbation of the paramagnetic spins by nearby paramagnetic ions is avoided. If the percentage of paramagnetic ions is less than 0.5%, the magnetic parameters are in general controlled by the symmetry of the crystal field at the site in which the paramagnetic ion is located. In such cases, the parameters can be explained using the "spin Hamiltonian" approach. More recently, considerable effort[1-5] has been dedicated to the study of samples in which the concentration of paramagnetic ions is increased to about 5%. In these studies, in addition to the usual spectra, new absorptions are visible which can be explained as arising from the exchange interactions when two paramangetic ions occupy nearby sites.

The study of pure paramagnetic salts via EPR at low temperatures has been very limited since the exchange effect in such salts is usually sufficiently large to lead to a ferromagnetic or antiferromagnetic state at low temperatures. Thus, the problem becomes one of studying a system with long range order in which the exchange effect is dominant. From the work of Giauque et al.[7,13-16] $NiSO_4 \cdot 6H_2O$ seemed to represent the somewhat unusual case of a paramagnetic salt which became neither ferromagnetic nor antiferromagnetic, even at very low temperatures. It seemed like an ideal material in which to study the intermediate case of the paramagnetic

ions with significant but not dominant exchange interactions. In addition the fact that the ground state was non-degenerate represented an interesting case of pure second-order paramagnetic material. Thus, $NiSO_4 \cdot 6H_2O$ seemed to present a particularly interesting system for study with EPR.

II. SURVEY OF PREVIOUS WORK

The hydrated salts of Ni^{2+} ($3d^8$, S = 1) have received considerable attention in the past.[8-10,19,20] Much of the work on $NiSO_4 \cdot 6H_2O$ was re-examined by Stout and Hadley.[11] The results of their work on the heat capacity of $NiSO_4 \cdot 6H_2O$ powder indicated that the ground state was split into three separate levels in which the upper two levels are 4.48 ± 0.07 cm^{-1} and 5.05 ± 0.07 cm^{-1} above the ground state. If the above splittings are written in the usual spin Hamiltonian notation, viz.

$$\mathcal{H}_s = g\beta \, \bar{H} \cdot \bar{S} + D \, S_z^2 + E(S_x^2 - S_y^2),$$

they give $D - E = 4.48$ cm^{-1} and $D + E = 5.05$ cm^{-1}. In addition to these values, however, it is also necessary to determine the g values and the angle ϕ, which is the angle that the magnetic z axis of a given site makes with the crystallographic c axis, and the size of the exchange and dipole-dipole interactions between the Ni^{2+} atoms (if they are sufficiently large). Stout and Hadley found $g_x = 2.216$, $g_y = 2.212$, $g_z = 2.181$, $\phi = 40.2$ best represented their data. However, these parameters do not describe their data perfectly. In order to fit the magnetic susceptability, it was necessary to include an exchange term in the spin Hamiltonian of the form, $\mathcal{H}_{ij} = \sum_{i \neq j} 2JzS_i \langle S_j \rangle$, where J is the exchange interaction constant, z is the number of nearest neighbors, and $\langle S \rangle$ is the expectation value of the spin angular momentum operator, thermally averaged over the states. Using the susceptibility data alone, it was found that $2J = -0.104$ cm^{-1} gave the necessary correction to the theoretical value of the susceptibility at liquid helium temperature. Analysis of earlier data taken by Watanabe[5] at low temperature in a similar manner gave $2J = +0.156$ cm^{-1}.

However, Stout and Hadley found that unless J=0, the temperature dependence of the susceptibility over a wider temperature region indicates that ϕ is not constant. The angle ϕ should remain constant since there are no phase transitions in this temperature range.[13] Also, the dipole-dipole interaction between Ni^{2+} may make a small but significant contribution to the susceptibility. We can conclude that the value of J is still uncertain.

More recently Giauque et. al.[7,13-16] have done extensive magneto-thermodynamic work. Using these results, Fisher and Hornung have arrived at a consistent set of spin Hamiltonian parameters which describe the magnetization and the heat capacity data of a single crystal of $NiSO_4 \cdot 6H_2O$ from 0 to 90 kG. They found excellent agreement when D = 4.741±0.001 cm^{-1} E = 0.01±0.06 cm^{-1}, and ϕ = 39.0. They also found that to fit the data exactly, an internal field correction of the form $\gamma \cdot M$ was necessary, where γ is a molecular field constant and includes both exchange and dipole-dipole contributions. This constant, γ, was found to be slightly anisotropic and equal to 0.266 moles/cm^3 along both the a-b bisector and the a axes and equal to 0.272 moles/cm^3 along the c axis.

The results of Giauque et al. are in the greatest disagreement with those of Stout and Hadley mainly as to the value of E. There is no doubt at all but that the heat capacity of the single crystal of Giauque is of much greater accuracy than is the powder work of Stout and Hadley. For this reason, one must conclude that the large E value found by Stout and Hadley is incorrect and that it only indicates the difficulty of obtaining energy levels from heat capacity measurements on polycrystalline samples.

If the molecular field approach is justified, then it is possible to use Moriya's[17] calculation to find the maximum J value possible such that no transition to a ferro or antiferromagnetic state is observed even at 0°K. (In all work to date, no such transition has been observed down to 0.4°K.) If one assumes that the x axis is the easy axis of magnetization, Moriya finds, using a molecular field model, that 2J must be less than D-E/z, or using Giauque et al.'s parameters, less than 1.2 cm^{-1}. While this calculation is crude, it can be expected to give a rough approximation of the maximum possible J that might be expected.

Bloembergen and Hou[18] have examined the effects of an electric field on the parameters D and E at liquid helium temperature. Their experiments are consistent with the work of Stout and Hadley. They examined the EPR spectrum of $NiSO_4 \cdot 6H_2O$ at K band at liquid nitrogen temperature and report an absorption at 6500±400 G when H_o was placed along the c axis. Attempts to reproduce this signal in the apparatus used in this thesis were unsucessful. Bloembergen and Hou also measured the magnetic susceptability along the a and c axes. They estimated that $2J = +0.104\ cm^{-1}$. It should be noted that Bloembergen and Hou do not describe the shape of their sample and were primarily concerned with the paramangeto-electric effect in $NiSO_4 \cdot 6H_2O$.

Of all the work carried out on $NiSO_4 \cdot 6H_2O$, that of Giauque et al. is the most comprehensive and detailed. However, relative to spectroscopic techniques, the sensitivity of the heat capacity measurements and the susceptibility should be much lower since it is necessary to obtain energy level data indirectly. In many respects, this is a distinct advantage

as the complexity of the unit cell and interatomic interactions in the $NiSO_4 \cdot 6H_2O$ system has repeatedly made analysis of a wide variety of spectra exceedingly difficult. Hartmann and Mullur[24] have examined the optical spectrum of $NiSO_4 \cdot 6H_2O$. The fitting of their spectra has been discussed by A. Bose and R. Chatterjee,[21] but beyond a general adjustment of the parameters, these workers had no success in assigning one or another of the major absorption bands (depending on how the various crystal field parameters are assigned). It is possible that the unusual absorption bands are due to collective effects such as excitons.

In this thesis the EPR spectrum of Co^{2+}, Mn^{2+}, and Cu^{2+} in $NiSO_4 \cdot 6H_2O$ are measured in the hope of further elucidating the nature of the spin-spin interactions in $NiSO_4 \cdot 6H_2O$. While it would appear that EPR should be ideally suited for the determination of such interactions, especially in the case of Mn^{2+}, the actual spectra are exceedingly complex. The EPR absorption for Ni^{2+} ions between the upper two energy levels was also observed in the hope of accurately determining E. The most obvious method of determining D and E is the direct observation of the far infrared absorption near 5 cm^{-1}. This also was carried out with interesting results. Several other types of experiments are possible. While most of them are theoretically appealing, some present formidable technical problems. The first is suggested by the work of Becquerral, van den Handel, and Kramers[22] and Levy and van den Handel,[23] (these workers found that within the experimental error, J=0 and D=2.74 cm^{-1} on the change of the rotation of the plane of polarization of light with change of magnetic field (Faraday effect)). While the Leiden workers used optical wave lengths, a similar

experiment could be carried out in the microwave region using the absorption observed in the EPR experiments. These data could be related to the susceptibility and the exchange interaction. A second possible experiment would be the direct observation of the NMR of a suitable diamagnetic impurity (e.g. $^{111}Cd^{2+}$ and $^{112}Cd^{2+}$) in the Ni^{2+} sites. This could, if detectable, offer a direct measure of the molecular field. The work of Giauque et al. has indicated that the spin-lattice relaxation of the proton is sufficiently short that the proton NMR should be easily detectable. However, since there are 48 inequivalent protons in a unit cell, these spectra might be exceedingly complicated. Thirdly, there is the possibility of following the temperature dependence of either the infrared or the EPR absorption spectra since the Boltzmann population varies considerably between 1.3 K and 4.2 K (Table I). Both of these were attempted. In the case of EPR, as discussed later, the intensity changes had appreciable effect on coupling and cavity Q. However, if each variable in the apparatus were carefully calibrated it should be possible to obtain more sensitive results from this approach.

TABLE I

Exicted State Population with D = 4.74 and E=0

Temperature (K)	Fraction in Excited States
1.2	0.007
2.0	0.062
3.0	0.17
4.0	0.28
∞	0.67

III. EXPERIMENTAL TECHNIQUES

A. X-Band Experiments

The EPR spectra were, in most cases, taken on a Varian V4502 spectrometer operating at X-band. All spectra were taken at 4.2°K or lower (down to 1.2°K) using apparatus constructed by D. W. Pratt. The addition of a pump with greater pumping speed allowed somewhat lower temperatures to be obtained (1.2°K with the Welch Duo seal 1307 versus 1.3°K with the previous arrangement). A nine inch Varian magnet with "Fieldial" unit (V-FR2503) was used in all but the experiments done at the high end of the X-band frequency region when a Pacific Electric Motor 12 inch magnet was used to attain a somewhat higher field. Since in all experiments with the Ni^{2+} ions we were not noise limited, a variety of microwave power sources were used in conjunction with simple EPR absorption spectrometers. A Polaroid variable frequency oscillator, Model 1207 whose frequency range was sufficiently high so as to allow some experiments at frequencies just above the X-band wave guide cut off was used in such configurations. Also, a Hewlett Packard sweep oscillator, Model 8690A was used in some experiments, as noted in Figs. 1 and 2. In general, however, the sepctrometer used was identical to that described in detail by D. W. Pratt in his low temperature experiments.

The measurement of the field and microwave frequency was accomplished by an external NMR and Hewlett Packard frequency counter. The NMR oscillator was a Harvey Wells FC-50° with a rebuilt power supply and a proton probe. The high field measurements were very difficult due to an increased absolute inhomogeneity in the field and due to the low signal

to noise ratio of the Harvey Wells instrument at high field. It was found necessary, upon sweeping through resonance, to move the magnet such that the NMR probe could be placed in the exact center ofthe field in order to get a detectable signal. While this would necessarily lead to some additional uncertainty with respect to reproducibility, since the high field Ni^2 absorptions were very wide, the uncertainty was small with respect to the natural errors in finding the center of the line. It might be added in this connection that the reproducibility of the "Fieldial" on the Varian Magnet at fields greater than 9000 G was detectable uncertain in field presumably due to heating of the windings and the power supply. It was found necessary to repeat a given measurement many times before the exact center of the line could be identified with real confidence.

B. Resonant Cavities

Two cylindrical microwave resonant cavities (Fig. 3) were constructed so as to have two convenient resonant frequencies (9.2 and 9.5 GHz when teflon filled) and the necessary dimensions to fit inside the liquid helium dewar with a mode such that the magnetic vector of the microwave field was oriented in a plane perpendicular to the plane defined by the laboratory magnetic field in all orientations (TE 011). Some difficulty was encountered in suppressing the excitation of the TM 011 mode which is degenerate with the TE 011 mode. Since the TM 011 mode has currents running from top to bottom of the cavity and the TE 011 mode does not, the insulation of the bottom of the cavity from the walls via a thin teflon wafer was successful in suppressing the undesired mode. A similar attempt to achieve the same end by painting the silver coupling windows was

unsuccessful due to the severe temperature changes causing peeling of the paint. It should also be noted that while a 7/16" coupling window was adequate in many experiments, the variable coupling apparatus designed by A. Jindo[26] was in general a great improvement. The resonant frequency of the cavities could be conviently lowered by the addition of quartz disc ($\sqrt{\epsilon} = 2$ for quartz as compared to $\sqrt{\epsilon} = 1.44$ for teflon) or raised by the removal of teflon.

In this way the frequency of the cavity could be varied over the full range of klystron in successive experiments quite easily. Several low frequency (S-band) experiments were attempted in the X-band apparatus by use of a coaxial cavity. A coaxial cavity with an unloaded Q of about two thousand was constructued, but upon addition of sample, the Q was sufficiently reduced so as to make detection of even the strong Ni^{2+} signal uncertain with the crude spectrometer we had set up. A second drawback in this case is that the magnetic component of the microwave standing wave is in the plane of the laboratory magnetic field, thus making the direction of H_1 with respect to H_o uncertain. A more useful approach, but one which would require more delicate engineering and impedance matching, is the traveling wave helix.

C. Sample Mounting

Initial studies were carried out on flat plates of $NiSO_4 \cdot 6H_2O$ single crystals provided by Semi-Elements Corporation. The crystals cleave conveniently into plates with the c-axis perpendicular to the plane of the plate. Experiments in the a-b plane were therefore easily accomplished. Experiments in the a-c plane required the construction of a crystal rotator. A small hole was drilled in the center of

the crystal plate and it was mounted on a quartz rod which in turn was mounted through a small hole in the cavity wall. The quartz rod was connected to a short lever arm which in turn was connected to a lever arm of identical length outside the liquid helium dewar. In this manner the crystal could be oriented in the desired plane by using the known facts about the crystallographic structure and the Co^{2+} resonances (assuming that the Co^{2+} ions were located in Ni^{2+} sites). The crystal rotator appears in Fig. 5.

A simple order of magnitude calculation indicates that shape effects in concentrated paramagnetic samples can be significant in the same way as in ferromagnetic resonance. Therefore, the g values obtained in the plates will be incorrect by a small but significant amount. In view of this a single crystal sphere 7 mm in diameter was machined and a small hole was drilled in it to a depth of 1/16". The sphere was mounted as in Fig. 4 with a glass rod glued in the hole. The crystal was then oriented by Professor K. Raymond with an X ray precession camera using the glass rod as a handle for adjustments. The accuracy of the mount was found to be $\pm 1^{\circ}$ or less for all orientations.

D. Temperature Measurements

Temperature measurement was accomplished via a carbon resistance thermometer and the vapor pressure of the liquid helium. The vapor pressure of the liquid helium was found to be sufficiently accurate for all experiments below $4.2^{\circ}K$. No attempt was made to control the temperature except by changing the pumping speed with a valve. At least 10 minutes elapsed before data were taken, after a small temperature change, in order that equilibrium could be established. If a much more

elaborate temperature control apparatus were available, more detailed information could have been obtained from such experiments.

E. K-band Experiments

Several K-band experiments were attempted using a bridge constructed by J. Tevebaugh[28] and the same simple spectrometer design as in Fig. 1. The frequency was varied from 19 GHz to 27 GHz. A very large dispersion signal was detected but no peak in absorption appeared over the field region 0 to 11 kG. at any frequency. It is presumed that this signal was due to bulk effect such as creation of phonons in the solid and not due to transitions at individual Ni^{2+} or Co^{2+} sites. They were therefore not examined in greater detail.

IV. CRYSTAL STRUCTURE

The crystal structure of α-$NiSO_4 \cdot 6H_2O$ was first determined by Beevers and Lipson[33] and subsequently discussed by Beevers and Schwartz.[34] The hydrogen bonds were assigned in a paper by O'Conner and Dale[35] on $NiSO_4 \cdot 6D_2O$ (via neutron diffraction analysis). All papers subsequent to the initial paper by Beevers and Lipson seem to follow Stout and Hadley's[11] description of the lattice which is with respect to the signs of ϕ. However, the errors do not affect the analysis of the heat capacity and magnetization data since the angle ϕ which alternates between $+\phi$ and $-\phi$ with respect to the c axis as one proceeds from one Ni^{2+} ion to the next along the c axis, enters their data as $\sin^2 \phi$ and no change results from the error in the sign of ϕ.

Figure 6 shows the projection in the a-b plane of four nations in one unit cell without sulfates or water. The arrows indicate the direction (projected in the a-b plane) of the magnetic z axis for each Ni^{2+} site. Each of the four Ni^{2+} ions in the unit cell is located at 0, 1/4, 1/2, 3/4 respectively of the length of the c axis, 18.305A. In the a-b plane the Ni^{2+} ions located at 0 and 1/2 are magnetically equivalent. Those located at 1/4 and 3/4 are also magnetically equivalent in the a-b plane. The above is also true for the a-c plane. In the a-b bisector, c-plane, the Ni^{2+} ions at 0 and 1/2 are equivalent but these at 1/4 and 3/4 are not.

The nearest neighbors form a tetrahedron about a given site. One possible theoretical model is, therefore, the four nearest neighbors forming a "quasi-unit cell" within which there is signficant exchange

interaction between the nearest neighbors and the central ion but not with those ions outside the unit. However, if the exchange interaction between Ni^{2+} ions is sufficiently large then it is necessary to include more than nearest neighbor exchange effects. Examination of the crystal structure indicates that there is a helix of nearest neighbors about the c axis and a set along the a and b axis arranged in such a manner that one alternates between the 0 Ni^{++} ion position and the 1/4 position in adjacent unit cells. These two chains of nearest neighbors should make the largest contribution to any long range exchange interaction.

The four nearest neighbors are 5.7 A from a given Ni^{2+} ion. The four next nearest neighbors are along the a and b axes and are 6.79 A from a given Ni^{2+} ion. A clearer picture of the details of the lattice can be obtained by examination of a model such as Fig. 7. Important lattice parameters are given in Table II.[33-35]

TABLE II

C = 18.305Å a=b = 6.79Å	x/a	y/b	z/c
0 Ni^{2+} (1)	0.7126	0.7126	0.000
1/4 Ni^{2+} (2)	0.7710	0.2080	4.576
1/2 Ni^{2+} (3)	0.2101	0.2101	9.152
3/4 Ni^{2+} (4)	0.2080	0.7710	13.728

V. Ni^{2+} MAGNETIC RESONANCE

A. Results and Discussion

The most intense feature of the EPR spectrum is observed in an X-band spectrometer close to 10 kG. This absorption is observed in single crystal when H_o is near the a-b bisector. It can also be observed in finely powdered samples of α-$NiSO_4 \cdot 6H_2O$. The position of the maximum in this absorption is very nearly the same in both the powder and in well oriented single crystals.

This absorption has a half width of about 1 kG at 4.2°K in the powder. A typical spectrum is given in Fig. 8. When the temperature is decreased to 1.3°K the width of the absorption decreases and there is a small shift in the maximum field position to lower field. This field shift is in the same direction as the change in bulk magnetization of the sample with temperature. This absorption was observed using frequencies ranging from 7.95 to 10.8. GHz. These results are summarized in Fig. 9.

In single crystals, when H_o is oriented aways from the a-b bisector the absorption decreases in intensity and shifts toward lower field. A splitting in this absorption can also be observed, but this effect will be discussed in a later section. Another major characteristic in the shifted absorption is a striking temperature dependence. About 10° away from the a-b bisector, lowering the temperature from 4.2 to 1.3°K causes a down-field shift of about 1 kG. This effect will also be discussed later.

Since the thermodynamic measurements of Giauque et al. can be accurately interpreted by assuming little or no interaction between the Ni^{2+}, it seems

reasonable that this intense absorption can also be interpreted with the same assumption. The Zeeman effect level spacings for isolated Ni^{2+} are shown in Figs. 10a,b,and c. The parameters in these figures are close to those evaluated by Fischer and Hornung.[7] With a quantum of 0.3 cm^{-1} and fields of 10 kG or less, it is quite apparent that no EPR transitions can be observed from the ground to either excited state. Transitions between the excited states could, however, give EPR absorptions in this range of fields. A clear experimental proof that this indeed was the case was shown by the temperature dependence of the spectrum. One would expect the intensity to vary directly with the relative Boltzman population of the two excited states. It was found to vary as predicted within experimental error, i.e. the intensity dropped markedly as the temperature was lowered by stages from 4.2°K to 1.3°K. This experiment confirmed the D parameter of Giauque et al. to within ± 0.5 cm^{-1}.

The temperature dependence of the intesnity of the Ni^{2+} absorption is a method by which the E and D value can also be determined with much greater accuracy than the ±0.5 cm^{-1} indicated above. However, much attention must be given to other variables in this experiment if there is to be any confidence in the results. Those things which could lead to false changes in intensity are: variations in power reaching the detector, variation in cavity coupling with temperature, variation in cavity Q factor. Feher[32] discusses the change in spectrometer sensitivity (using cyrstal diode detectors) as a function of cavity coupling. He shows, and we have confirmed, that coupling between 50-80% of the microwave power into the cavity has only a slight effect on sensitivity. Since it is possible to adjust coupling to within ±1%, this should not be a limiting

source of error. The same resetability is possible with power reaching the diode, if one uses sensitive attenuators and a micro-ammeter connected to the detector. The only assumption necessary, therefore, is that Q is essentially constant over the temperature range of the experiment. The electrical properties of the cavity are indeed nearly constant, but those of the sample are not. In fact, since we are dealing with a concentrated sample of paramagnetic ions, whose properties are changing rapidly with temperature, the sample itself can change Q by more than a small amount if it is a large sample. However, if a small sample is used, much more reliable values of D and E can be obtained by this method.

B. Isolated Ion Theory

In order to quantitatively assign the observed transitions, it is necessary to first develop the spin Hamiltonian formalism as applied to Ni^{+2} in a distorted octahedron. It has been shown[29] that a transition metal ion with S=1 in a site with rhombohedral symmetry can be described by a spin Hamiltonian of the following form:

$$\mathcal{H} = (\beta \sum_{i}^{x,y,z,} g_i H_i S_i) + DS_z^2 + 1/2E (S^{+2} + S^{-2})$$

For S=1 we can immediately write down the matrix resulting from this Hamiltonian which is appropriate to the case that $D > g\beta H$:

	$\psi(0)$	$\psi(-1)$	$\psi(+1)$
$\psi(0)$	0	$\frac{\beta[g_x H_x - i g_y H_y]}{\sqrt{2}}$	$\frac{\beta[g_x H_x + i g_y H_y]}{\sqrt{2}}$
$\psi(-1)$	$\frac{\beta[g_x H_x + i g_y H_y]}{\sqrt{2}}$	$D - \beta g_z H_z$	E
$\psi(+1)$	$\frac{\beta[g_x H_x - i g_y H_y]}{\sqrt{2}}$	E	$D + \beta g_z H_z$

where 0, -1, +1 correspond to the quantitization of S along z. If one applies a two by two rotation of the above matrix via the unitary transformation, T, one can obtain the E elements on the diagonal where T has the following form:

$$T = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & -\sin\theta \\ 0 & \sin\theta & +\cos\theta \end{pmatrix}$$

And thus,

$$T^{-1} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{pmatrix}$$

where $\tan 2\theta = E/\beta g_z H_z$, the Hamiltonian matrix becomes:

	$\psi(0)$	$\psi-$	$\psi+$
$\psi(0)$	0	$\frac{\beta g_x H_x(\cos\theta - \sin\theta)}{\sqrt{2}}$ $\frac{i\beta g_y H_y(\cos\theta+\sin\theta)}{\sqrt{2}}$	$\frac{\beta g_x H_x(\cos\theta+\sin\theta)}{\sqrt{2}}$ $\frac{i\beta g_y H_y(\cos\theta-\sin\theta)}{\sqrt{2}}$
$\psi-$	$\frac{\beta g_x H_x(\cos\theta-\sin\theta)}{\sqrt{2}}$ $\frac{i\beta g_y H_y(\cos\theta+\sin\theta)}{\sqrt{2}}$	$D-\beta g_z H_z \cos 2\theta$ $-E \sin 2\theta$	0
$\psi+$	$\frac{\beta g_x H_x(\cos\theta+\sin\theta)}{\sqrt{2}}$ $\frac{i\beta g_y H_y(\cos\theta-\sin\theta)}{\sqrt{2}}$	0	$D+\beta g_z H_z \cos 2\theta$ $+ E \sin 2\theta$

Where $\psi^- = \psi(-1) \cos\theta - \psi(+1) \sin\theta$

$\psi^+ = \psi(-1) \sin\theta + \psi(+1) \cos\theta$

For experiments with H_0 in the a-b plane, H_1 is directed along the c axis in our cylindrical cavities. We wish to calculate the transitions between the two excited states, ψ^+ and ψ^-. The intensity of such a transition is proportional to $\cos^2\phi \mid \langle\psi^+ \mid S_z \mid \psi^-\rangle\mid^2$ since S_z is the only component of S connecting ψ^+ and ψ^-. Thus,

$$I \propto \mid\langle\psi(-1) \cos\theta - \psi(+1) \sin\theta \mid S_z \mid \psi(+1) \cos\theta + \psi(-1) \sin\theta\rangle\mid^2$$

$$I \propto (2 \sin\theta \cos\theta)^2 \cos^2\phi = \sin^2 2\theta \cos^2\phi$$

but since $\tan^2 2\theta = \dfrac{\sin^2 2\theta}{1 - \sin^2 2\theta}$

$$I \propto \frac{E^2}{(g_z \beta H_z)^2 + E^2} \cdot \cos^2\phi$$

In the a-b plane $H_x = H \cos\alpha$ and $H_y = H \sin\alpha$ where α is measured from the y axis which corresponds to the a-b bisector.[30]

Then

$$H_{y_2} = H_{y_4} = H_o \cos\alpha \qquad H_{y_1} = H_{y_3} = H_o \sin$$

$$H_{x_2} = -H_{x_4} = -H_o \sin\alpha \cos\phi \qquad H_{x_1} = H_{x_3} = H_o \cos\alpha \cos\phi$$

$$H_{z_2} = -H_{z_4} = -H_o \sin\alpha \sin\phi \qquad H_{z_1} = H_{z_3} = H_o \cos\alpha \sin\phi$$

where 1, 2, 3, 4 designated the four magnetically non-equivalent Ni^{2+} sites. It is obvious that for $\alpha = 0$ there will be an absorption with a relative intensity

$$I \propto \frac{E^2}{(g_z \beta H)^2} \cot^2\phi$$

for site 1 and 3, and $I \propto \cos^2\phi$ for sites 2 and 4, if $g_z\beta H \gg E$. Since in the a-b plane site 1 and 3 are related to 2 and 4 by a 90° rotation in the a-b plane, it is expected that asone rotates through 90° the

allowed absorption from sites 1 and 3 will steadily diminish in intensity as α approaches 90°, while those due to sites 2 and 4 will steadily increase in intensity as α approaches 90°. This will give a spectrum in the a-b plane with an apparent periodicity of 90°.

Having established that the excited state transition is indeed allowed, it remains to show its explicit angular dependence as H_o is rotated in the a-b plane. In order to do this approximately we apply perturbation theory to second order on the general matrix (1), and we find the energy difference between the two excited levels:

$$\Delta\epsilon = \frac{2\beta g_z H_z \cos 2\theta + 2E \sin 2\theta}{D} - \frac{\left(\beta g_\perp\right)^2 (H_x^2 + H_y^2)(\beta g_z H_z \cos 2\theta + E \sin 2\theta)}{D^2} + \frac{\left(\beta g_\perp\right)^2 (H_z^2 - H_y^2) \sin 2\theta}{D}$$

where we have assumed $D \gg E$ and $g_x = g_y = g_\perp$

Substituting for $\cos 2\theta$ and $\sin 2\theta$, and simplifying we obtain

$$\Delta\epsilon = \frac{1}{\sqrt{E^2 + (g_\parallel \beta H_z)^2}} \left[2(g_\parallel \beta H_z)^2 + 2E^2 - \frac{(\beta g_\perp)^2 (H_y^2 - H_x^2)E}{D} \right]$$

Not let $(H_y^2 - H_x^2) = Hf_2(\alpha,\phi)$ and $H_z^2 = Hf_1(\alpha,\phi)$, where α is the angle between the a-b bisector and the H_o direction, and ϕ is the angle between the site z axis and the c axis. Making the above substitutions and solving for H, we obtain the following:

$$H^2 = \frac{-4KE^2 + \Delta\epsilon^2 (g_\parallel\beta)^2 f_1(\alpha\phi)^2 \pm \Delta\epsilon \sqrt{\Delta\epsilon^2 (g_\parallel\beta)^4 f_1(\alpha\phi)^4 + 4KE^2 (K - 2(g_\parallel\beta)^2) f_1(\alpha,\phi)}}{2K^2}$$

where

$$K = \frac{2(g_\parallel\beta)^2 f_1(\alpha,\phi)^2 D + (g_\perp\beta)^2 f_2(\alpha,\phi)^2 E}{D}$$

Inserting for the a-b plane, the relations

$$f_2(\alpha,\phi) = \sin^2\alpha - \cos^2\alpha \sin^2\phi$$

$$f_1(\alpha,\phi) = \cos^2\alpha \cos^2\phi$$

It is immediately noticed that for most angles, many terms are small and can be dropped and the angular dependence in the a-b plane can be easily evaluated.

TABLE III

	H(gauss)/sites 2 and 4	
$\alpha = 0°$	2250	$\nu = 8.90$ GHz
$\alpha = 30°$	2580	$D = 4.74\ cm^{-1}$
$\alpha = 45°$	3160	$E = 0.03\ cm^{-1}$
$\alpha = 60°$	4390	$g = 2.24$
$\alpha = 75°$	6530	
$\alpha = 90°$	10120	

The situation is not so simple in the (a-b bisector) - c plane, but since:

$$H_{y_1} = H_{y_3} = H_y$$

$$H_{x_1} = H_{x_3} = H_z \sin\phi$$

$$H_{z_1} = H_{z_3} = H_z \cos\phi$$

$$H_{x_2} = H_y \cos\phi - H_z \sin\phi$$

$$H_{y_2} = H_{y_4} = 0$$

$$H_{x_4} = -H_z \sin\phi - H_y \cos\phi$$

$$H_{z_2} = H_z \cos\phi + H_y \sin\phi$$

$$H_{z_4} = H_z \cos\phi - H_y \sin\phi$$

where

z = c axis

y = a-b bisector

and α is the angle between H and the c axis

and ϕ is the angle between the site z axis and the c axis

TABLE IV

	H(gauss)/sites 2 and 4 in (ab bisector) c-plane	
$\alpha = 0°$	1832	$\nu = 9.01$ GHz
$\alpha = 30°$	2115	$D = 4.74\ cm^{-1}$
$\alpha = 45°$	2590	$E = 0.03\ cm^{-1}$
$\alpha = 60°$	3735	$g = 2.24$
$\alpha = 75°$	6620	
$\alpha = 90°$	10200	

In a manner similar to that used for the a-b plane, the relative intensity of the absorption spectra of ions in the (a-b bisector) - c plane can be calculated using the above components of H_o. It is seen that for the 2 and 4 sites of the unit cell there is 0 intensity for all α and again a single transition should be observed at very low intensity at the c axis and rising to a maximum intensity at the a-b bisector (Table II).

A brief examination of the data taken in the a-b plane and the (a-b bisector) - c plane, indicates that qualitatively and semi-quantitatively, the isolated ion approximation gives a satisfactory explanation of the data (Figs. 11 and 12).[37] The quantitative agreement is not as good as that obtained from data in which the isolated ion approximation is more easily justified, e.g. paramagnetic ions in diamagnetic lattices. If one uses the relative intensity equation to calculate the value of E,

one obtains (Figs. 13 and 14) from the a-b plane data the value E = 0.08±0.02 cm^{-1} and from the (a-b bisector) - c plane the value E = 0.06±0.02 cm^{-1}. These values do not give a particularly exact fit to the experimental results. In fact these values represent an over-estimate of the size of E since the cavity Q and the coupling are reduced considerably when the absorption becomes very strong. The result of this effect is to reduce the measured intensity near the a-b bisector axis. The values of E obtained by this method should be regarded as an upper limit to the size of E, rather than accurate measurements.

If E is very small one would expect the absorption intensity to fall off very quickly as one rotates a few degrees away from the a-b bisector axis in any direction. This gives a plausible explanation for the narrowness of the powder spectra, namely that E is much smaller than $g_z \beta H_z$ at most orientations. Thus, if one assumes in the isolated ion approximation, that all absorption intensity comes from the a-b bisector orientation, then it is a simple matter to calculate the predicted frequency versus field dependence of the absorption spectra for various E values. This was done by Jane Schell.[30] Using the data obtained from $NiSO_4 \cdot 6H_2O$ powder and these calculations, one obtains an E value of ±0.03 cm^{-1} as the best fit of the data (Fig. 9). This, however, should represent a lower limit to the E value since the apparent peak will be drawn to a somewhat lower field by the absorptions arising from orientations of the particles in the powder at angles near but not exactly along the a-b bisector axis. When the single crystal data taken with H_o oriented along the a-b bisector axis, the value of E necessary to obtain a best fit was found to be 0.035 cm^{-1}. For comparison, the value E = 0.07 cm^{-1} yielded a value for Ho which was 20% smaller than the observed field

of 10.4 kG. While the angular dependence of the spectra in the a-b or the a-b bisector c planes can not be perfectly fit with the inclusion of the exchange interaction, the best possible fit was obtained in the isolated ion approximation with $E = 0.035 \pm 0.005$ cm^{-1}.

An experiment was also carried out to see if the measured E value was temperature dependent. The spectrum was measured at 4.2°K and at 1.3°K at various angles in the a-b plane and the relative intensities were compared.. It was found that the E value was temperature independent over this range within experimental error.

If one replaces all near neighbors of a given Ni^{2+} by point dipoles and calculates the net field resulting according to β/r^3 taking into account the relative sign of each contribution, one finds that the correction is much too small to explain the difference between the isolated ion model calculations and the data. The major source of these differences must lie in the exchange coupling between the Ni^{2+} ions.

VI. MAGNETIC RESONANCE, TRANSITION METAL ION IMPURITIES

A. Co^{2+}

The ESR spectrum of Co^{2+} impurity in $NiSO_4 \cdot 6H_2O$ was first observed as a natural impurity in single crystal samples grown by Semi-Elements Corporation for Giauque et al. It was quicly assigned to Co^{2+} via its characteristically anisotropic g values and eight line hyperfine splitting ^{59}Co I = 7/2. The g anisotropy results from the admixture of some excited state transforming as $^4T_{2g}$ to the ground $^4T_{1g}$ state. The effect of the admixture on the g valueswas studied by Abragam and Pryce.[38] and more recently by Thornley et al.[39] Since there are no data available on the excited states of Co^{2+} in $NiSO_4 \cdot 6H_2O$, none of the necessary parameters (such as 10 Dq) are known with sufficient accuracy to justify a crystal field calculation of the anisotropy. The usual spin Hamiltonian approach, for effective spin 1/2, was applied. The Hamiltonian in such a case is:

$$\mathcal{H} = \sum_{i}^{x,y,z} g_i \beta H_i \cdot S_i$$

Since the Co^{2+} spectra showed the symmetry of the lattice (e.g. all sites equivalent along the a axis and the c axis), it was concluded that Co^{+2} ions were in Ni^{2+} sites. Also, spectra in the a-b and a-c planes indicated that the Co^{2+} sites had axial symmetry and therefore the spectra could be fitted by two g values, $g_{\parallel}$ and $g_{\perp}$. Initial spectra where taken in flat plates of $NiSO_4 \cdot 6H_2O$ since the single crystals conveniently cleave into such plates with the c axis perpendicular to the plane of the plate. A good fit of the data could not be obtained with the parameters available. A simple calculation shows that one reason for this is a shape effect due to the fact that the Co^{2+} ions are in a paramagnetic lattice which has a considerable bulk magnetization.

Yager and Bozorth[40] showed that when H_o is perpendicular to a thin plate $h\nu = g\beta (H_o - 4\pi M)$ where ν = resonant frequency, β = Bohr magneton, g = spectroscopic splitting factor and M is the magnetization of the sample at the given orientation and temperature of the experiment.

If one uses Giauque et al.'s published values of M, one obtains a correction of about 35 G in field due to the shape of the sample when H_o is along the ca axis. For H_o in the plane of a this plate, $h\nu = g\beta \times [H_o (H_o + 4\pi M)]^{1/2}$ it is found that the correction for H_o along the a axis is of the opposite sign to the correction for H_o along the c axis and also for about 35 G. This correction was too small to significantly improve the description of the experimental data with adjustable parameters. However, since there is no shape effect in spherical samples, a spherical ball of $NiSO_4 \cdot 6H_2O$ was shaped and mounted as described above. It was found that when the shape effect was calculated for the flat plate with H_o along a and H_o along c, the results were only correct to about 20%. The errors are due to the fact that the above equations assume an idealized thin plate whereas the actual samples were sufficiently small in diameter as to be significantly thick with regard to their length and breadth. The two sets of g values are:

Plate	Sphere
$g_a = 4.741$	$g_a = 4.688$
$g_c = 4.246$	$g_c = 4.301$

In order to obtain a fit of the angular dependence of the g values in the a-b and the a-c planes, the following procedure was used. Since[41]

$$g(\theta) = \sqrt{g_{\parallel}^2 \cos^2\theta - g_{\perp}^2 \sin^2\theta}$$

or

$$g(\theta) = \sqrt{(g_{\parallel}^2 - g_{\perp}^2)\cos^2\theta + g_{\perp}^2}$$

where θ is the angle between H_o and the site z axis, we can show from the lattice geometry that

$$g_{ab}(\alpha) = \sqrt{(g_{\parallel}^2 - g_{\perp}^2)\sin^2\theta\cos^2(45 + \alpha) + g_{\perp}^2}$$

where in the a-b plane, α is the angle between H_o and the a axis and ϕ is the angle between the site z axis. The sites 1 and 3 are related to the sites 2 and 4 by a 90° rotation in the a-b plane. Therefore, if α gives g for sites 1 and 3 then $\alpha + 90°$ gives g for sites 2 and 4 at a given orientation of H_o.

For the a-c plane

$$g_{ac}(\alpha) = \sqrt{(g_{\parallel}^2 - g_{\perp}^2)(\cos\alpha\cos\phi \pm \sqrt{2}/2 \sin\alpha\sin\phi)^2 + g_{\perp}^2}$$

where α is the angle between H_o and the c axis and ϕ is the same as in the a-b plane. The (+) sign corresponds to the 1 and 3 sites and the (-) sign corresponds to the 2 and 4 sites for a given orientation of H_o. If one takes the derivative of g_{ac} with respect to α and sets the result equal to zero, one finds that a maximum in g occurs in the a-c plane when

$$\tan\alpha = \sqrt{2}/2 \tan\phi.$$

From the data taken in the a-c plane, a maximum in g occurs when H_o is at an angle of 51.5° with respect to the c axis. This yields an angle of ϕ for Co^{2+} opms pf 60.7°. The angle ϕ for Ni^{2+} is, according to Giauque et al., 39°. This difference is quite considerable, and it is somewhat surprising since one might expect Co^{2+} to fit rather well into a Ni^{2+} site and to give a similar orientation of the magnetic axes. However,

as will be shown below, large exchange effects are involved in the description of the angular dependence of the Co^{2+} g values, and they are probably the explanation of the large difference for ϕ.

A spectrum taken in a powdered sample of Co^{2+} doped $NiSO_4 \cdot 6H_2O$ gave a set of eight weak but clearly defined lines centered at g = 6.444. At g is 3.3 - 3.0 there were several much stronger but unassignable absorptions. It was concluded that g = 6.444 corresponded to $g_{\parallel}$ and that $g_{\perp}$ corresponded to the region of the unassigned absorption. Since $g_{\parallel}$ and ϕ were then known, the $g_{\perp}$ value was quickly obtained using the measured g value of 4.688 in the spherical sample when H_o was along the a axis. The result for $g_{\perp}$ was 3.162. The a-c plane and a-b plane field dependence as a function of H_o orientation was then calculated. The low field absorption agreed reasonably well with the calculated g value as shown in Figs. 15 and 16. However, in the vicinity of the minimum g value, in both planes the fit is poor. An examination of the lattice shows that this was to be expected, since at the maximum field in both the a-c and a-b planes, the g value should correspond to $g_{\perp}$. The two maxima are different by about 300G so that clearly the Hamiltonian used to describe the spectra is too simple.

The effect which we have thus far neglected is that caused by the magnetization of the individual Ni^{2+} ions in the crystal. If we assume that the effect of the magnetization is isotropic, we can use as a first approximation the "molecular field"[42] model in which the resonance field, H , is considered to be the sum of the laboratory magnetic field, H_o, and a field arising from the magnetization, H_E. H_E is defined as $H_E = \gamma M$, where γ is a constant independent of temperature and M is

the magnetization per unit volume. However, a brief examination of the data indicates that if one adjusts the data by this means in the a-c plane, it requires that γ be positive, whereas in the a-b plane it must be negative. While it is possible to continue to use this model with more than one γ value, it is more useful to consider the exchange effects with a more specific model.

If it is assumed that each Co^{2+} is surrounded by a tetrahedron of Ni^{2+} ions, then a calculation similar to the one carried out previously for the far infrared spectrum of Ni^{2+} should yield the most reasonable 1^{st} order correction to the isolated ion calculation of the g values. Since the Zeeman effect must be included, this calculation was judged to be beyond the scope of this thesis. Therefore, the simpler case of an exchange coupled Co^{2+} - Ni^{2+} pair has been carried out in Appendix I in order to explain, at least qualitatively, the effect of exchange on the g value. The results indicate that the exchange interaction causes a shift in the g values which is of the order of magnitude $2Jg_{Ni}/\ D+E$. If an orientation of H_o different from that used in the appendix assumed the correction is smaller. This would imply that for a correction to g of about $|0.2|$ $|J|$ must be of the order of 0.2 cm^{-1}. While this is not an unrealistic value it does not offer any explanation for the change in sign of J necessary to explain the a-c and a-b plane data. Only a much more sophisticated model which considers 1-1, 2-3 and 1-2 type interactions (see Chapt. VII for explanation of nomenclature) will fully explain the exchange effects.

The angular dependance of the hyperfine interaction is described by the terms $A_{\parallel} I_z S_z$ and $A_{\perp} (I_x S_x + I_y S_y)$ in the spin Hamiltonian. The selection for the hyperfine transitions are $\Delta M_I = 0$, $\Delta M_S = \pm 1$. To the

1st order this leads to 2I + 1 equally spaced absorptions. The angularly dependent energy separation between absorptions is given by KM_I

where

$$K^2 = \frac{A_{\parallel}^2 g_{\parallel}^2 \cos^2\theta + A_{\perp}^2 g_{\perp}^2 \sin^2\theta}{g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta}$$

Since the nucleus is surrounded by a nearly spherically symmetric electron cloud, it should be expected that J would have a considerably smaller effect on $A_{\parallel}$ and $A_{\perp}$ than on $g_{\parallel}$ and $g_{\perp}$. At first glance it might appear that the angular dependence of K would then provide a useful method to determine the correctness of values. However, quadrupole interaction and second-order hyperfine terms sufficiently complicate the hyperfine angular dependence that small errors in g cannot be isolated. If $A_{\parallel}$ is assigned the value 232×10^{-4} cm^{-1} and $A_{\perp} = 29.5\times10^{-4}$ cm^{-1} the angular dependence of the hyperfine splitting between the levels corresponding to $M_I = 1/2$ (in which case the second order effects are minimized) is satisfactorily explained to an accuracy of about 3%. This is illustrated in Fig. 17.

The magnitude, sign and symmetry of the Co^{2+} - Ni^{2+} exchange interaction is a problem of considerable interest. However, the highly anisotropic g values, the highly anisotropic A values, quadrupole interaction, etc. make confident assignment of the spin Hamiltonian parameters to a highly degree of accuracy very diffcult. This fact makes J correspondingly more uncertain. The value J is not negligible, however, and, as in the case of Ni^{2+} - Ni^{2+} interaction, $|J| \sim 0.2$ cm^{-1}.

B. Mn^{2+}

In addition to the Co^{2+} impurity in the $NiSO_4 \cdot 6H_2O$ lattice in the sample provided by Semi-Element Coroporation, a very complicated spectrum

was observed in the vicinity of g = 2. When H_o was placed along the a-b bisector, the spectrum appeared in its simplest form. At this orientation there were five clearly identifiable sets of six equally spaced and equally intense lines. The number of lines and their separation suggested that the impurity was Mn^{2+}. A new single crystal was grown with a small amount of Mn^{2+} ion as an intentional impurity. The resulting spectra confirmed the assignment of the previously obtained spectra to Mn^{2+}. If the usual spin Hamiltonian for Mn^{2+} is used (with the assumption that a is small with regard to D), then it may be written in the following way:

$$\mathcal{H} = g \beta H \cdot S + D (M_S^2 - 35/12) + A M_I \cdot M_S$$

All attempts to fit the spectra with this Hamiltonian failed. At angles away from the a-b bisector, the spectra became even more complicated by additional splitting. At the a-b bisector, one should expect from the above Hamiltonian, five sets of ten lines arising from each of the two magnetically inequivalent Ni^{2+} sites. Only half this number was observed. If H_o is placed along the a axis where all sites are magnetically equivalent, then the g value obtained from the center of the sphere is about 2.3. This large shift from 2.0 for Mn^{2+} suggests that J is large, since D should symmetrically split the Mn^{2+} about a center at g = 2. If it is presumed that the principal effect of exchange interaction is to change g and that the primary source of the width of the spectrum is due to D (with minor additional splittings due to J), then the spectral width indicates that D must be 0.1 cm^{-1}.

If the most intense and least anisotropic set of six lines is assigned to MS= $\pm 1/2$, this leads to a value of D = 0.15 cm^{-1}. However if D is the dominant term, then the set of five absorptions (ignoring hyperfine splittings)

should be symmetrically arranged about the most intense set of lines. This was not found to be the case; the most intense set occurred at the low field end of the spectra.

In order to show that the $D < g \beta H$ and that the lines arise from $\Delta M_s = \pm 1$ transitions, the frequency dependence of the absorptions was measured. It was found that at the a-b bisector, the slope of the line resulting from a plot of ν vs. H_o for each of the lines corresponded roughly to that expected for $\Delta M_s = \pm 1$ transitions. It can thus be said that D, if the usual spin Hamiltonian parameters are applicable , is less than 0.3 cm^{-1}.

C. Cu^{2+}

In the course of K-band experiments on Mn^{2+}, additional four-line spectra were observed in the a-b plane. It was assigned to Cu^{2+} impurities in the Ni^{2+} sites. With the addition of a-b bisector - c plane angular dependence, it was found by A. Jindo that the g values which best fit the spectra are $g_{\parallel} = 2.890$ and $g_{\perp} = 2.481$. The agreement between the predicted and the actual angular dependence for Cu^{2+}, like Co^{2+}, was not perfect. In addition, it is clear that the g values are shifted by about 0.3 from their usual values in diamagnetic lattices of $g_{\parallel} = 2.4$ and $g_{\perp}$ 2.1. This indicated that $|J|$, in the case of Cu^{2+}, is on the order of 0.3 cm^{-1} and it is most probably negative in value.

VII. FAR INFRARED MEASUREMENTS

The infrared spectrum of a sample of $NiSO_4 \cdot 6H_2O$ was examined from 3 cm^{-1} to 25 cm^{-1} at 4.2 K with a spectrometer designed by Professor P. L. Richards[36] and operated by George Brackett. A 10 mil mylar beam splitter was used in conjunction with a polyethylene grating filter whose cut off occurred at 27 cm^{-1}. A series of experiments were also carried out between 1.31 K and 1.35 K by pumping on the liquid helium (250 data points were taken over a 25 cm^{-1} range). A magnetic field of up to 50 kG was attained via a superconducting solenoid. The field was oriented such that it was parallel to the c axis of the crystal. Two different flat plate single crystal samples were used. At 4.2°K three absorptions were seen when the magnetic field was applied. The first absorption was assigned to the transition from the ground state to the lower excited state, the second to the transition from the ground state to the upper excited state, and the third to a transition between the two excited states. Due to the fact that the intensity of the IR light source was very low below 4 cm^{-1}, the transition between the excited states was visible only when H_o was greater than 25 kG. At 1.3 K the two excited states were sufficiently depopulated that the transition between the two excited states was no longer detectable at any field strength.

At zero field a broad asymmetrical absorption was observed at both 4.2°K and 1.3 K (Figs. 18 and 19). At 1.3 K the absorption was much more sharply peaked, but the line width remained nearly constant. There is some evidence of structure at 1.3 K, but it is not clearly defined. The absorption at zero field corresponds to the transition from the

$M_s = 0$ ground state to the $M_s = \pm 1$ excited levels. The peak of the absorption correspond to the spin Hamiltonian D value only if J and E are almost equal to 0. The peak occurred at 4.63 cm^{-1}, 4.56 cm^{-1}, and 4.63 cm^{-1} in the three experiments at 4.2 K. At the 1.3 K the peak occurred at 4.51 cm^{-1} in two separate experiments. The weighted mean center was constant at 4.70 cm^{-1} ±.02 cm^{-1} at both temperatures.

The most interesting feature of the spectra was the large width which is independent of temperature. In addition, the peak is considerably different from the value of D predicted by Giauque et al. for an isolated ion. Both of these facts indicate that J is not negligible and must be several tenths of a wave number.

The effect of the exchange interaction on the spectroscopically measured D value can be seen if it is assumed that the exchange interaction is sufficiently large for atoms along the a or b axis to justify an exciton model for the description of this exchange interaction. In this approximation for a chain of identical atoms separated by the distance a, the energy levels in the zero field are $\epsilon(K) = D \pm E + J_e \cos(Ka)$ (Where K is defined as the wave vector of the exciton as it moves through the crystal). The usual selection rule for a transition from the ground state to an exciton state in such a system is K = 0. With this restriction, the only allowed absorption is $\Delta\epsilon = D \pm E + J$. If E is small, then the spectroscopically observed absorption corresponds to D and J_e and not the true D value determined by Giauque et al. The heat capacity data of Giauque et al indicated a D value based on a hypothetical single excited state at the center of the exciton band. As long as J_e is reasonably small with respect to D, then this represents a good approximation.

TABLE V. Splittings measured by infrared spectroscopy

Table Va. $\Delta\epsilon$ = Separation between ground state and lower excited state in cm^{-1} (averaged)

H_o	$\Delta\epsilon$
0 (kG)	4.70
5	4.14
10	3.95(?)
15	3.75(?)
20	(?)
30	3.8(?) 4.0(?)
40	4.25
50	4.82

Table Vb. $\Delta\epsilon$ = Separation between ground state and upper excited state in cm^{-1}

H_o	$\Delta\epsilon$
0 (kG)	4.70
5	4.95
10	5.54
15	6.18
20	6.82
30	8.40
40	10.15
50	11.9(?)

Table Vc. $\Delta\epsilon$ = Separation between two excited states in cm^{-1}

H_o	$\Delta\epsilon$
30 (kG)	4.74
40	6.00
50	7.20

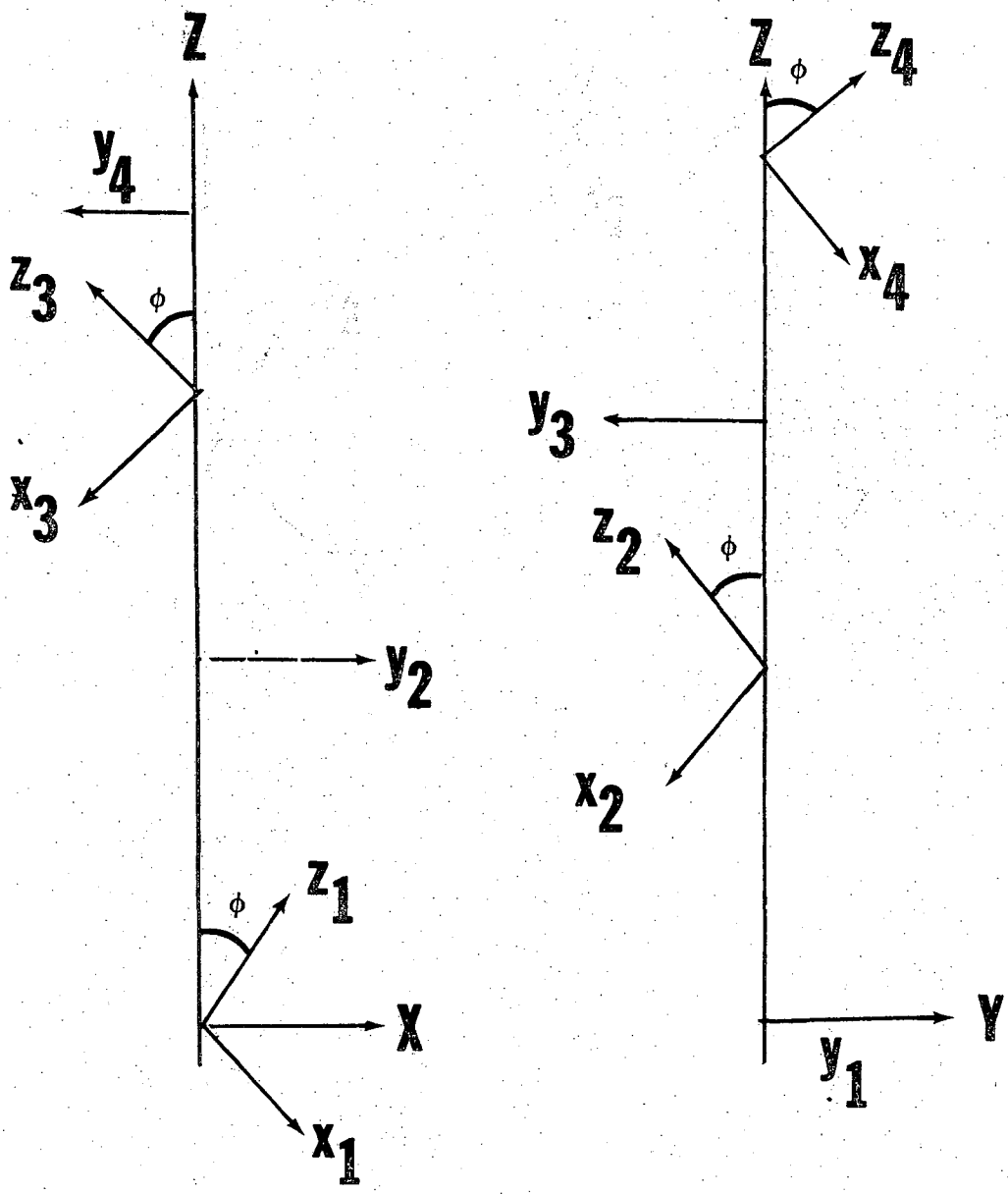
The field dependence of the absorptions are presented in Table Va, Vb and Vc. It can be seen that agreement with Giauque et al. is reasonably good, as shown in Fig. 20. At low fields, however, the agreement is not excellent in the case of the ground to lower excited state transition. While it is possible that the low spectrometer sensitivity in the region of 3.5 cm^{-1} to 4.5 cm^{-1} is the cause, it is more likely that this is due to exchange interaction of sufficient size as to be significant with respect to the Zeeman energy at low fields. Several different model calculations have been carried out in order to explain these deviations. On the basis of these models, qualitative explanations of the observed deviations from the results expected from the isolated ion model, can be obtained. Two limiting cases are seen. One is the case of the strong exchange coupling, leading to an exciton-like conception of the electron in the excited state of a particular Ni^{2+}. It is unlikely that such a model represents the primary Ni^{2+} ion interaction since it usually implies a large exchange interaction ($J_e > 10$ cm^{-1}), and one would expect to see a splitting in the infrared absorption at zero field. The observation of a ferromagnetic or antiferromagnetic state at very low temperature would also be expected if the interaction is very large. However, for J_e of intermediate size (~0.3 cm^{-1}), this model might still offer a useful description of some observed effects. In addition, for J_e less than about 1 cm^{-1}, no splitting or long range ordering of spins at low temperature would be expected. The most successful model for a first approximation was deemed to be weak exchange coupling between nearest neighbors. The near-tetrahedral "coordination" of nearest neighbor Ni^{2+} ions about a given central Ni^{2+} in the lattice suggests itself as the basis for such a calculation.

The crystal structure consists of sheets of identical Ni^{2+} with these sheets parallel to the a-b plane. Each Ni^{2+} in these sheets has its z axis rotated down from the c axis by the angle $+\phi$. The rotation in each plane is along the y axis of each sheet. There are four such sheets and the y axis of each sheet corresponds to the a-b bisectors. The sheets are arranged so that the y axes form a spiral along the c axis.

The Ni^{2+}-Ni^{2+} interactions within each sheet are between identically oriented Ni^{2+} and will be called 1-1 interactions. The 1-1 interactions are between next nearest neighbors and may be fairly large since they are between identical Ni^{2+} ions. As noted previously, these ions effect all excited states in the same way and their spectroscopically measured effect is indistinguishable from D. They will be neglected in the "tetrahedral" model calculation. Interactions between the sheets will be of the type 1-2, 1-3, and 1-4. While the 1-3 and 1-4 are surely non-zero, they can be neglected in this model since they should be very small. All of the nearest neighbors yield exchange interactions of the type 1-2.

In the far infrared, these 1-2 interactions form the basis for Davydov splittings in the spectrum. Since its Zeeman effect of the 1 sites and 2 sites are different (except along a, b or c), the 1-2 interaction should be observed in the EPR.

In order to perform the calculation we set up the following coordinate system: the laboratory Z axis corresponds to the c axis, the laboratory Y and X axes correspond to the two perpendicular a-b bisector. Disregarding translation from the Z axis the 1-2 sites appear as follows:


Z
y4
z3
φ
x3
y2
φ
z1
X
x1
Z
φ
z4
x4
y3
z2
φ
x2
y
y1

Then the components of S in the laboratory coordinate system are related to the components of S in the site coordinate system in the following way:

$$S_{Z_1} = S_{z_1} \cos\phi - S_{x_1} \sin\phi \qquad S_{Z_1} = S_{z_2} \cos\phi - S_{x_2} \sin\phi$$

$$S_{X_1} = S_{x_1} \cos\phi + S_{z_1} \sin\phi \qquad S_{X_2} = S_{y_2}$$

$$S_{Y_1} = S_{y_1} \qquad S_{Y_2} = -S_{x_2} \cos\phi - S_{z_2} \sin\phi$$

$$S_{Z_3} = S_{z_3} \cos\phi - S_{x_3} \sin\phi \qquad S_{Z_4} = S_{z_4} \cos\phi - S_{x_4} \sin\phi$$

$$S_{X_3} = - S_{x_3} \cos\phi - S_{z_3} \sin \qquad S_{X_4} = - S_{y_4}$$

$$S_{Y_3} = - S_{y_3} \qquad S_{Y_4} = S_{x_4} \cos\phi + S_{z_4} \sin\phi$$

The basic Hamiltonian used to describe this system is of the following form:

$$\mathcal{H} = \sum_i \mathcal{H}_{io} + \sum_{i \neq j} \mathcal{H}_{ij} + \sum_i \mathcal{H}_i (H)$$

where H_{io} is the isolated Ni^{2+} ion Hamiltonian, $H_i(H)$ describes the Zeeman interaction and H_{ij} is the exchange term. The index i denotes the site, from 1 to 4, in the unit cell corresponding to a given Ni^{2+} ion. H_{ij} has the following form for 1-2 interactions in which the exchange is isotropic:

$$\mathcal{H}_{12} = J \, \vec{S}_1 \cdot \vec{S}_2$$

In the site coordinate system, we obtain

$$S_1 \cdot S_2 = S_{z_1} S_{z_2} \cos^2\phi - (S_{z_1} S_{x_2} + S_{x_1} S_{z_2}) \sin\phi \cos\phi + (S_{z_1} S_{y_2} - S_{y_1} S_{z_2}) \sin\phi + i \frac{S_1^+ S_2^- - S_1^- S_2^+}{2} \cos\phi + S_{x_1} S_{x_2} \sin^2\phi$$

If we consider the very low temperature case where the excited state is almost depopulated, then upon absorption of an infrared quantum by one of the ions only one ion will be in the $M_s = \pm 1$ levels. In this case all of the terms in $\bar{S}_1 \cdot \bar{S}_2$ are zero except the last two. This is the simplest possible case and will be called the "1^{st} order approximation" since it neglects terms of the magnitude of J/D.

The ground state wave function is simply:

$$\Psi(0) = \psi_2(0)\ \psi_1(0)\ \psi_{1'}(0)\ \psi_3(0)\ \psi_{3'}(0)$$

where we have labeled the central ion 2, the nearest neighbor below the central ion, 1 and 1', and the nearest neighbor above the central ion 3 and 3'. Since the 3 and 3' are exactly equivalent, then first order wave functions are

$$\Psi_3^{\pm}(\pm 1) = \frac{\psi_3(0)\ \psi_{3'}(\pm 1) \pm \psi_3(\pm 1)\ \psi_{3'}(0)}{\sqrt{2}}$$

and similarly for 1 and 1'

$$\Psi_1^{\pm}(\pm 1) = \frac{\psi_1(0)\ \psi_{1'}(\pm 1) \pm \psi_1(\pm 1)\ \psi_{1'}(0)}{\sqrt{2}}$$

these can be combined with $\psi_2(\pm 1)$ to give

$$\Psi_\alpha(\pm 1) = \psi_2(\pm 1)\ \psi_1(0)\ \psi_{1'}(0)\ \psi_3(0)\ \psi_{3'}(0)$$
$$\Psi_\beta^{\pm}(\pm 1) = \psi_2(0)\ \Psi_1^{\pm}(\pm 1)\ \psi_3(0)\ \psi_3(0)$$
$$\Psi_\gamma^{\pm}(\pm 1) = \psi_2(0)\ \psi_1(0)\ \psi_{1'}(0)\ \Psi_3^{\pm}(\pm 1)$$

the matrix elements are then (in the 1^{st} order approximation)

$$\langle \alpha(\pm 1) | \mathcal{H} | \beta^{+}(\pm) \rangle = [\langle 0_1, 0_{1'}, \pm 1_2 | \mathcal{H} | 0_1, \pm 1_{1'}, 0_2 \rangle$$
$$+ \langle 0_1, 0_{1'}, \pm 1_2 | \mathcal{H} | \pm 1_1, 0_{1'}, 0_2 \rangle] / \sqrt{2}$$
$$= \mp 2i J \cos\phi + J \sin^2\phi$$

and

$$\langle \alpha(\pm 1) \,|\mathcal{H}_{ij}|\, \gamma^{+}(\pm 1) \rangle = \frac{\mp 2i\, J \cos\phi + J \sin^2\phi}{\sqrt{2}}$$

$$\langle \alpha(\pm 1) \,|\mathcal{H}_{ij}|\, \beta^{-}(\pm 1) \rangle = 0$$

$$\langle \alpha(\pm 1) \,|\mathcal{H}_{ij}|\, \gamma^{-}(\pm 1) \rangle = 0$$

$$\langle \alpha(\pm 1) \,|\mathcal{H}_{ij}|\, \beta^{+}(\mp 1) \rangle = \frac{J \sin^2\phi}{\sqrt{2}}$$

$$\langle \alpha(\pm 1) \,|\mathcal{H}_{ij}|\, \gamma^{+}(\mp 1) = \frac{J \sin^2\phi}{\sqrt{2}}$$

since $\bar{S}_1 \cdot \bar{S}_3$ are neglected

$$\langle \beta(\pm 1) \,|\mathcal{H}_{ij}|\, \gamma(\pm 1) \rangle = 0$$

and elements of the type $\langle \gamma(\pm 1) \,|\mathcal{H}_{o}|\, \gamma(\mp 1) \rangle$ are all equal E and similarly those of the type $\langle \gamma(\pm 1) \,|\mathcal{H}_{o}|\, \gamma(\pm 1) \rangle = D$. Thus the Hamiltonian matrix for the (+) levels is:

	$\beta(+1)$	$\gamma(+1)$	$\alpha(+1)$	$\alpha(-1)$	$\gamma(-1)$	$\beta(-1)$
$\beta(+1)$	D	0	a+b	b	0	E
$\gamma(+1)$	0	D	a+b	b	E	0
$\alpha(+1)$	-a+b	-a+b	D	E	b	b
$\alpha(-1)$	b	b	E	D	a+b	a+b
$\gamma(-1)$	0	E	b	-a+b	D	0
$\beta(-1)$	E	0	b	-a+b	0	D

where $a = 2i\, J \cos\phi$

$$b = \frac{J \sin^2\phi}{\sqrt{2}}$$

If one applies a suitable transformation the false degeneracy of the diagonal terms can be lifted and the Hamiltonian matrix takes the following form:

	$\beta(-1)$ $-\beta(+1)$	$\alpha(-1)$ $-\alpha(+1)$	$\gamma(-1)$ $-\gamma(+1)$	$\beta(-1)+\beta(+1)$ $-\gamma(-1)+\gamma(+1)$	$\beta(-1)+\beta(+1)$ $\gamma(-1)+\gamma(+1)$ $-\alpha(-1)-\alpha(+1)$	$\beta(-1)+\beta(+1)$ $\gamma(-1)+\gamma(+1)$ $\alpha(-1)+\alpha(+1)$
$\beta(-1)$ $-\beta(+1)$	D-E	0	0	0	$\frac{+a}{\sqrt{2}}$	$\frac{-a}{\sqrt{2}}$
$\alpha(-1)$ $-\alpha(+1)$	0	D-E	0	0	a	a
$\gamma(-1)$ $-\gamma(+1)$	0	0	D-E	0	$\frac{a}{\sqrt{2}}$	$\frac{-a}{\sqrt{2}}$
$\beta(-1)+\beta(+1)$ $-\gamma(-1)-\gamma(+1)$	0	0	0	D+E	0	0
$\beta(-1)+\beta(+1)$ $\gamma(-1)+\gamma(+1)$ $-\alpha(-1)-\alpha(+1)$	$\frac{-a}{\sqrt{2}}$	-a	$\frac{-a}{\sqrt{2}}$	0	D+E-2$\sqrt{2}$b	0
$\beta(-1)+\beta(+1)$ $\gamma(-1)+\gamma(+1)$ $\alpha(-1)+\alpha(+1)$	$\frac{a}{\sqrt{2}}$	-a	$\frac{a}{\sqrt{2}}$	0	0	D+E+2$\sqrt{2}$b

If it is assumed that the infrared radiation strikes the surface of the crystal such that the magnetic component of the radiation is perpendicular to the c axis, then the intensities of magnetic dipole transition from the ground state to exchanged coupled excited levels can be estimated. There is a small magnetic component of the infrared radiation along the c axis but it should be less than 10% and will be neglected as a first approximation. The intensities of the transitions will be proportional

to $|\langle\Psi_0|\ S_X\ |\text{excited state}\rangle|^2$ and $|\langle\Psi_0|\ S_Y\ |\text{excited state}\rangle|^2$. The transition to states which are composed of linear combinations of the wave function belonging only to site 1 and/or site 3 ions will be neglected since the central ion energy levels and their perturbations by the 1 and 3 ions are the purpose of the calculation. If the magnetic component of the infrared radiation is directed along the x axis of the central ion, then, $(1/2)|\langle 0|S_y|-1\rangle - \langle 0|S_y|+1\rangle|^2 = 1$ and transitions to the two remaining states containing components of site 2 wave functions are not allowed. If, however, the magnetic component of the radiation is directed along the Y axis, then transition to the states

$$\frac{\alpha(-1)+\alpha(+1)}{\sqrt{2}} \quad \mp \quad \frac{\beta(-1)+\beta(1)+\gamma(1)+\gamma(-1)}{2}$$

is allowed with intensity proportional to $\cos^2\phi$. In this case, the transition to the

$$\frac{\alpha(+1)-\alpha(-1)}{\sqrt{2}}$$

state gives zero intensity. Since the magnetic component of the radiation is randomly oriented in the X-Y plane, the intensity of transition to the three excited states arising from site 2 is found to be 1 for the state with energy D-E (to 1^{st} order) above the ground state and $\cos^2\phi$ for the states at energies $D+E\pm 2J\sin^2\phi$ above the ground state.

The theoretical "1^{st} order approximation" is valid only in the case in which one atom is excited in the tetrahedron of Ni^{2+} atoms. This is best approximated experimentally by the infrared spectrum at 1.3 K(Fig. 17). The spectrum at 4.2K is similar in appearance but is broadened (Fig. 18) at the peak of the absorption. If the high field absorption is used (in

which case the exchange interaction is only a small perturbation on the Zeeman energy) as a model for the most intense line, then an explanation of the asymmetry of the infrared absorption at 1.3 K can be obtained. If the angle ϕ is assumed to be 39° from the data of Giauque et al., and the line widths of the less intense absorptions are assumed to be the same as the more intense absorptions, then the line shape and intensity of the less intense absorption can be approximated. Using these three absorptions the observed single absorption can be obtained. It is found that the best approximation to the spectrum occurs when the three absorptions are located at 4.50 cm^{-1} (intensity 1), 4.55 cm^{-1} (intensity $\cos^2 \phi$), and 4.87 cm^{-1} (intensity $\cos^2\phi$). If E is assumed to be 0.035 cm^{-1} from the magnetic resonance data, one obtains from the difference in energy of the two less intense lines (to 2^{nd} order) the value of $J = +0.12$ cm^{-1}. When this value of J is used in conjunction with $E = 0.035$ cm^{-1} and $D = 4.74$ cm^{-1}, it is seen that the predicted absorptions all occur at about 0.2 cm^{-1} above the actually observed absorption. This can be attributed to the exchange interaction between the central ion and those which lie in the same plane but lie in different crystallographic unit cells. These ions include the next nearest neighbors and are coplanar with a given Ni^{2+}. Since all of the coplanar ions are oriented in the same way as the ion at the center of the tetrahedron, it would not be surprising if such exchange interaction is of roughly the same size as that for the nearest neighbor exchange interaction. Also, since the coplanar ions are all oriented in the same way, the effect of the exchange interaction is exactly diagonal in Hamiltonian matrix and thus indistinguishable from D. Therefore the "D" in the tetrahedral model calculation

is not the same as that of Giauque et al., since it does not contain the exchange interaction due to the coplanar ion. It is thus possible to obtain the value $J_e = +0.20\ cm^{-1}$ as the contribution to the spectroscopically measured D due to the exchange interaction between equivalent Ni^{2+} ions.

The effect of J upon the field dependence of the spectra should be noticeable but the calculation in this case is immensely more difficult even if the exchange between only two Ni^{2+} is calculated rather than the full tetrahedron of five Ni^{2+} atoms. However, such a calculation might explain qualitatively the small difference between the isolated ion Zeeman effect and experiment.

VIII. THE EFFECT OF EXCHANGE ON THE EPR SPECTRUM OF Ni^{2+}

The far infrared spectrum, in the absence of a strong magnetic field, is senstive to exchange interactions between the Ni^{2+} in non-equivalent sites. In the presence of a strong magnetic field these same exchange interactions become second order and the only remaining first order exchange effects are between Ni^{2+} in equivalent sites. With the selection rule $\Delta K = 0$ for EPR transitions between the exciton states we are left with only second-order contributions from exchange interactions between nonequivalent sites. It is not too difficult to do an exchange coupled pair calculation in the presence of a magnetic field. The best way to approach the calculation is to start with the Zeeman effect calculation for an isolated Ni^{2+}. This is, in general, a 3×3 matrix and it can be diagonalized to any degree of accuracy. If one now uses these eigenvectors as a basis set it is then possible to add the exchange Hamiltonian and to determine both first and second order terms due to exchange. As a practical matter, we have only been able to do this for a limited number of field orientations for a pair of Ni^{2+} ions and for a limited accuracy for the 3×3 Zeeman Hamiltonian.

Two effects were observed, in the course of attempts to determine the value of E, which could not be described by an isolated ion model. When the field was rotated away from the a-b bisector axis in either the a-b plane or the a-b bisector -c plane, the single absorptions, described previously in the single ion calculation, split into two components of unequal intensity. Initially it was assumed to be due to a slight mis-orientation of the crystal; however, careful mounting of the sample showed

this not to be the case. When the angular dependence of the absorption was measured in the a-b plane at 4.2 K and at 1.3 K, the field dependence of the absorption as a function of angle was different for the two temperatures at all angles except the a-b bisector axis.

Upon examination of the ions in the unit cell, it is noted that the 1 and 3 ions are related by a rotation of 180° in the a-b plane and by a change in ϕ from $+\phi$ to $-\phi$. It might then be expected that a splitting might arise from the concomitant changes in sign for matrix elements between the 2-3 ions, and the 1-2 ions. A detailed calculation shows that this is indeed the case for at least one of the first-order matrix elements. However a truly quantitative explanation of this splitting awaits a more detailed calculation with a more exact diagonalization and with the inclusion of second order terms. The temperature dependence of this splitting is not too difficult to explain. When the field is oriented along the a-b bisector, there are essentially no terms which give a field induced exchange interaction. This is confirmed by the EPR spectrum for there is no temperature dependence that can be detected for this Zeeman splitting. The γ parameter used by Giauque et al. would indicate that the field should shift by several hundred gauss from 1.3 K to 4.2 K and no such shift is observed. When the field is rotated away from the a-b bisector, this is no longer true and we find large matrix elements which correspond to a field induced exchange interaction. From 1.3 K to 4.2 K we find by experiment that the field can shift by 1000 G. This shift is now larger than the parameter of Giauque et al. would indicate. Our calculations are sufficiently crude, however, that we can not extract a value for J from the observed shift.

In addition to the direct effect of exchange upon the Ni^{2+} EPR absorption, it was noted that there appeared at low field (H_o was in the a-b bisector -c plane) at least one addition absorption . This absorption was of much lower intensity than the high field absorption. If the exchange coupling of Ni^{2+} ions is not negligable as shown above, it is not difficult to see that each excited state will be split into several energy levels. Since EPR experiments obey the selection rule $\Delta M_s = \pm 1$, most transitions among these levels will be nearly forbidden. It is highly probable that these nearly forbidden transitions are the explanation for this weak absorption. A Jindo[43] has found the location of this weak absorption to be highly dependent on the orientation of H_o, as should be expected for such transitions. Since this absorption arises directly from exchange splittings, it should provide a very sensitive method for determining the value of J directly.

ACKNOWLEDGEMENTS

I considered for a time entitling this final footnote to my thesis the "dis-acknowledgement". I felt it was as important for me to acknowledge the aching inadequacies of this educational experience as it was to acknowledge those who supported me while it was taking place. While such a critique is badly needed, it seems rather late in the game for me to attempt it. I arrived at a time when the problems of mass education were being put into sharp focus by the FSM. Those problems have since been largely put aside unsolved. The harvest of such neglect can only be an increasingly "tumultuous" future. The price for failing to answer the cry for radical changes is going higher each year. How much longer can it be ignored?

On a more positive note, it is a pleasure to say thanks to Rollie for his enthusiastic support. Dave, Jim, Aki, Tony, Raymond, Tom and Joyce have all added immeasurably to the enrichment of my life and to the quality of this work, and I thank each of them for their particular contribution. To Gale and Betsy, I can not begin to express the gratitude I feel for what you have added to my life and this work.

In addition, I would like to acknowledge the able work of George Brackett who gathered the Infrared data and to Professor K. Raymond who oriented the nickel sulfate crystal sphere.

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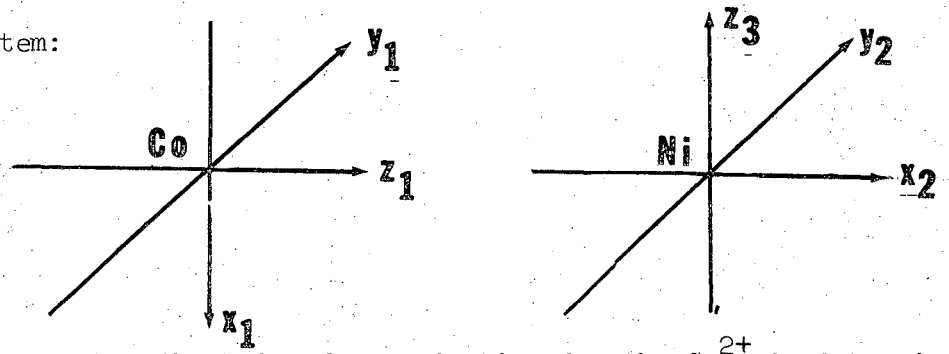
APPENDIX I

THE THEORY OF FIELD INDUCED EXCHANGE

While a realistic calculation using the tetraheral model is exceeding ingly tedious, the nature of the Co^{2+} - Ni^{2+} interaction can be shown using a simple pairwise exchange interaction between a Co^{2+} and a Ni^{2+} with H_o along the a-b bisector. We use sites 1 and 2 with the following coordinate system:



This assumes that the axis of quantization for the Co^{2+} is determined by H_o (Paschen-Bach Effect) and Ni^{2+} remains determined by the crystal field. For convenience it will be assumed that the two coordinate systems are not tilted with respect to one another. The exchange Hamiltonian can then be immediately written as:

$$\mathcal{H}_{12} = J_{12}\ S_1 \cdot S_2 = S_{z_1} S_{x_2} - S_{x_1} S_{z_2} + S_{y_1} S_{y_2}$$

$$= 1/2\ [S_{z_1} (S_2^{+} + S_2^{-}) - (S_1^{+} + S_1^{-})\ S_{z_2}]$$

$$-1/4\ (S_1^{+} - S_1^{-})\ (S_2^{+} - S_2^{-})$$

The wave functions can be written as simple product wave functions of the following form:

$$\psi_1(\pm 1/2)\ \psi_2(0),\ \psi_1(\pm 1/2)\ \psi_2(+1),\ \psi_1(\pm 1/2)\ \psi_2(-1)$$

However, since the Ni^{2+} excited state wave functions are nearly degenerate (assume E is small) the proper linear combinations must be written for them

as follows:

$$\psi^{\pm} = \frac{\psi_{(+1)} \pm \psi_{(-1)}}{\sqrt{2}} .$$

Thus the correct product states are $\psi_1(\pm 1/2)\ \psi_2(0)$, $\psi_1(\pm 1/2)\ \psi_2^{+}$ and $\psi_1(\pm 1/2)\ \psi_2^{-}$. The matrix elements of each of these states can then be easily obtained. In addition, there exist non-zero elements arising from the Zeeman interaction and the D and E terms of the Ni^{2+} ions. The spin Hamiltonian has the form

$$\mathcal{H}_{spin} = g_1 \beta\ H_o \cdot S_1 + g_2 \beta\ H_o \cdot S_2 + D\ S_z^{\,2} + E(S_x^{\,2} - S_y^{\,2})$$

Then

	$(-1/2,0)$	$(+1/2,0)$	$(-1/2,\psi^{-})$	$(+1/2,\psi^{-})$	$(-1/2,\psi^{+})$	$(+1/2,\psi^{+})$
$(-1/2,0)$	$-g_1\beta H/2$	0	0	$+J/2$	$g_2\beta H - J/2$	0
$(+1/2,0)$	0	$g_1\beta H/2$	$-J/2$	0	0	$-g_2\beta H + J/2$
$(-1/2,\psi^{-})$	0	$-J/2$	$D-E - g_1\beta H/2$	$-J/2$	0	0
$(+1/2,\psi^{-})$	$+J/2$	0	$-J/2$	$D-E + g_1\beta H/2$	$-J/2$	0
$(-1/2,\psi^{+})$	$g_2\beta H - J/2$	0	0	$-J/2$	$D+E - g_1\beta H/2$	0
$(+1/2,\psi^{+})$	0	$g_2\beta H + J/2$	0	0	0	$D+E+g_1\beta H/2$

From the above matrix, second order perturbation theory gives the following energies for the exchange perturbed Co^{2+} states:

$$\epsilon(+1/2,0) = \frac{g_1\beta H}{2} - \frac{J^2}{4(D-E-g_1\beta H)} - \frac{(g_2\beta H + J/2)^2}{D+E}$$

and

$$\epsilon(-1/2,0) = -\frac{g_1\beta H}{2} - \frac{J^2}{4(D-E+g_1\beta H)} - \frac{(g_2\beta H - J/2)^2}{D+E}$$

or

$$\Delta\epsilon = \epsilon(1/2,0) - \epsilon(-1/2,0) = g_1\beta H - \frac{2J\ g_2\ \beta H}{D+E} - \frac{J^2\ g_1\ \beta H}{2(D-E)^2}$$

or

$$\Delta\epsilon = g\beta H$$

where

$$g = g_1 - \frac{2J\, g_2}{D+E} - \frac{J^2\, g_1}{2(D-E)^2} .$$

FIGURE LIST

1. Block diagram of EPR spectrometer for 4-8 GHz.
2. Block diagram of EPR spectrometer for 8-12 GHz with frequence source locked to cavity.
3. Cylindrical Teflon-filled X-band resonant cavity.
4. Small cylingrical Teflon mount to hold spherical ball samples. The notches allow slight expansion around the ball for a snug fit. The ball is attached to a 1/16" rod which fits into the hole along the axis of Teflon cylinder. The cylinder fits into the cavity shown in Fig. 3 and its axis is horizontal.
5. Method used to rotate crystal plates at liquid helium temperatures.
6. Projection of four unit cells of α-$NiSO_4 \cdot 6H_2O$ on the ab plane. The arrouws show relative directions of z axis of Ni^{2+} spin Hamiltonian.
7. Photograph of crystal model of α-$NiSO_4 \cdot 6H_2O$ showing only Ni^{2+} and SO^{4-} ions. The four unit cells are viewed with the c axis vertical.
8. Absorption spectrum at 4.2°K and 8.7185 GHz with magnetic field along the ab bisector. The spectrum of a powder sample is almost identical to this one.
9. Resonance frequency vs. field position of Ni^{2+} absorption with magnetic field along the ab bisector. The dots are experimental values at both 4.2 and 1.3°K and the curves are drawn for (a) $E = 0.03\ cm^{-1}$, the molecular field parameter $\gamma = 0$ and (b) $E = 0$, $\gamma = 0.266$ given by Fisher and Hornung.[7] Here we see that the introduction of E rather than γ gives a better fit.

10. Zeeman energy levels of an isolated $Ni(H_2O)_6^{2+}$ triplet.
    (a) magnetic field pointed along z axis of the spin
    (b) H_0 along x axis
    (c) H_0 along y axis.
11. Angular dependence of Ni^{2+} absorption in the (ab bisector) - c plane. α is the angle between H_0 and c axis. The dots are the field positions observed with a spherical sample at 1.3°K and the squares at 4.2°K. The curve is calculated using the approximate equations given in the text for an isolated Ni^{2+} ion in 2, 4 sites with D = 4.74 cm^{-1} and E = 0.03 cm^{-1}.
12. Angular dependence of Ni^{2+} absorption in the ab plane. Points correspond to the calculated field positions for an isolated Ni^{2+} ion.
13. Intensity vs. orientation in the ab plane. The angle α is from the ab bisector in the ab plane. Black circles and spheres are experimental values at 4.2°K and 1.3°K respectively. The curves are drawn from calculated values of E = 0.08 cm^{-1} and E = 0.06 cm^{-1} at 4.2°K.
14. Intensity vs. orientation in (ab bisector) - c plane. The dots represent the experimental points and the solid curve is drawn for the best fit to the observed values. The dotted curves are the calculated values with (a) E = 0.035 cm^{-1} (b) E = 0.06 cm^{-1} (c) E = 0.08 cm^{-1}.
15. Field position vs. angle for Co^{2+} spherical sample in the ab plane. The center of hyperfine lines is plotted against the magnetic field orientation in this plane. Points are experimental, while the curve is calculated.

16. Co^{2+} ac plane spectra. The angle α is between the magnetic field and the c axis.

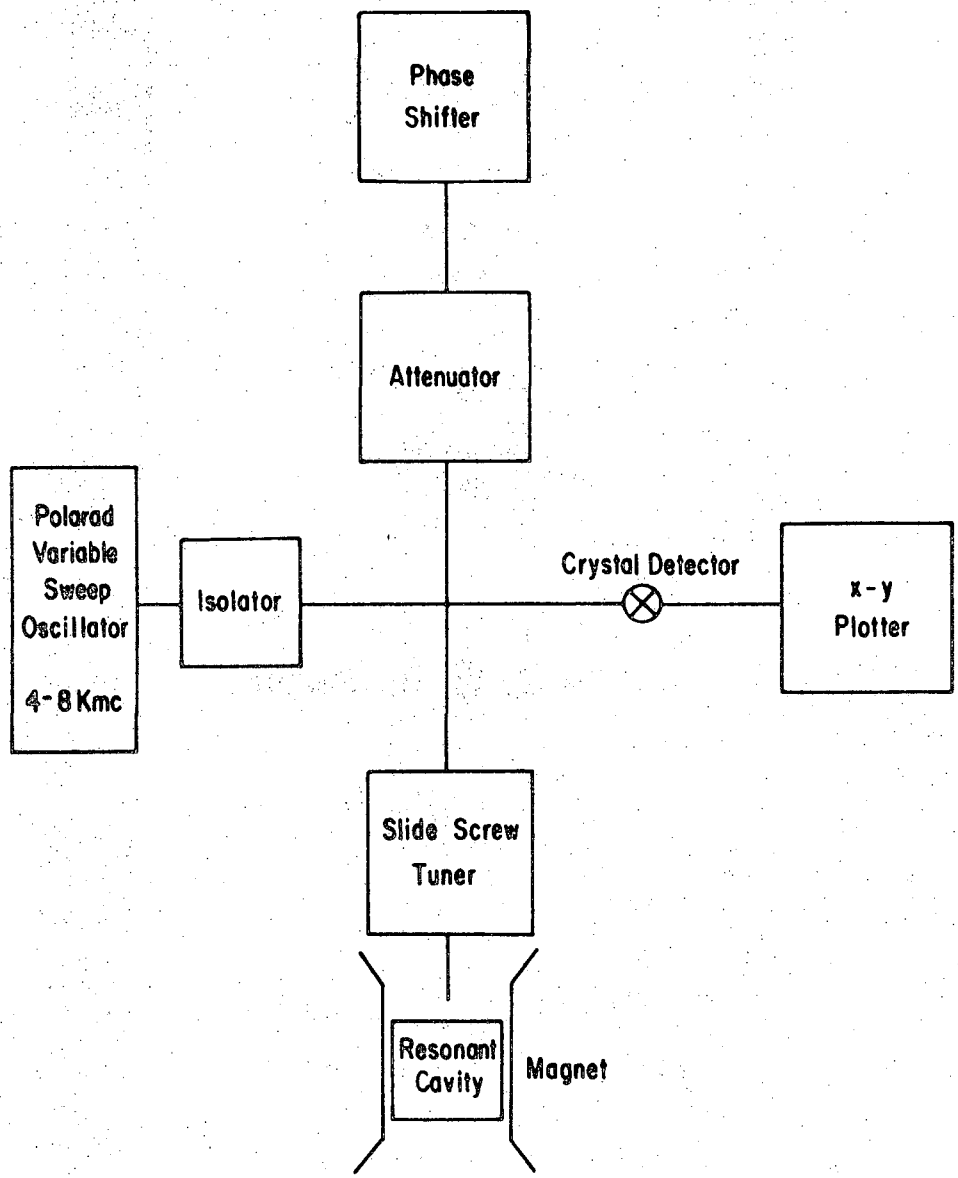
17. Angular dependence of Co^{2+} hyperfine splitting in the ab plane. The calculated curve is obtained from

$$g_{\parallel} = 6.44, \quad g_{\perp} = 3.162$$
$$A_{\parallel} = 232\times10^{-4}\,cm^{-1}, \quad A_{\perp} \simeq 30\times10^{-4}\,cm^{-1}$$
$$\phi = 60.7^{\circ}$$

18. Infrared absorption spectrum of α-$NiSO_4 \cdot 6H_2O$ at $4.2^{\circ}K$ and zero magnetic field. F and H stands for the D value reported by Fisher and Hornung.[7] The horizontal arrow indicated the resolution of the infrared instrument.

19. Infrared absorption spectrum of α-$NiSO_4 \cdot 6H_2O$ at $1.3^{\circ}K$.

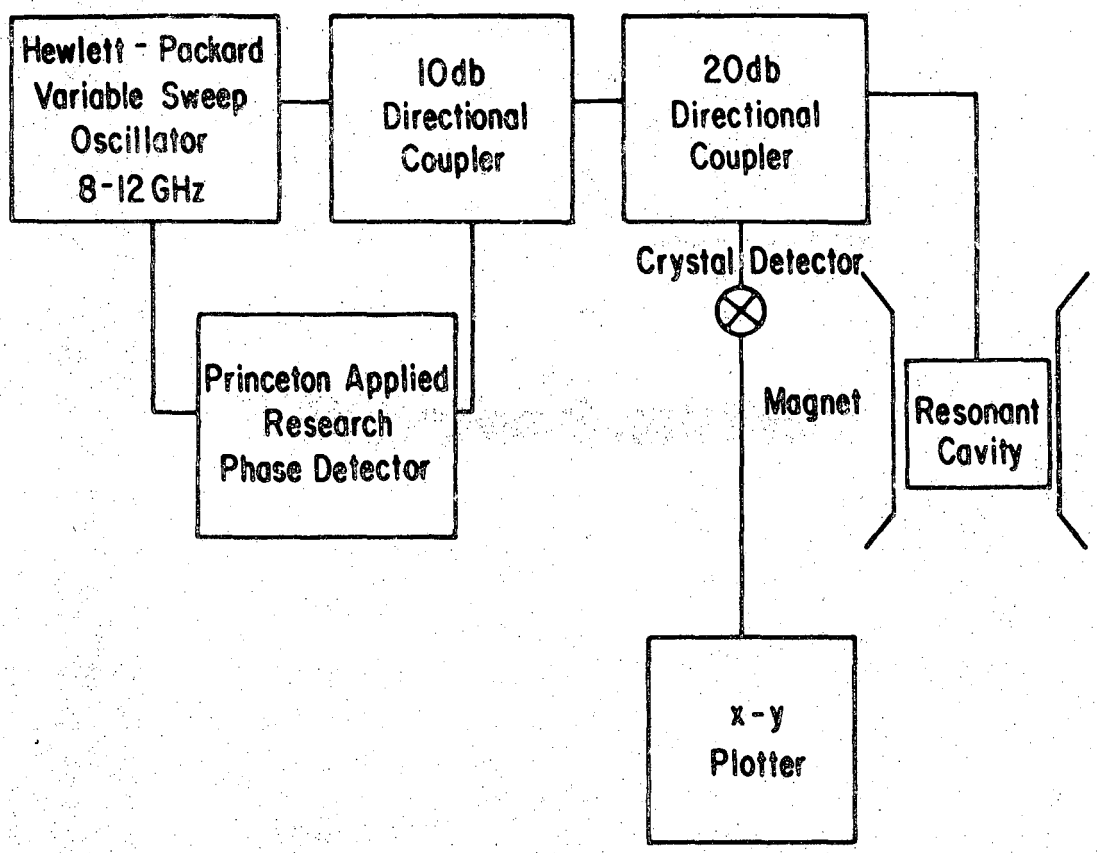
20. Comparison of infrared and thermodynamic results for Zeeman splitting of the two excited states of Ni^{2+}.



Absorption Spectrometer

XBL 703-468

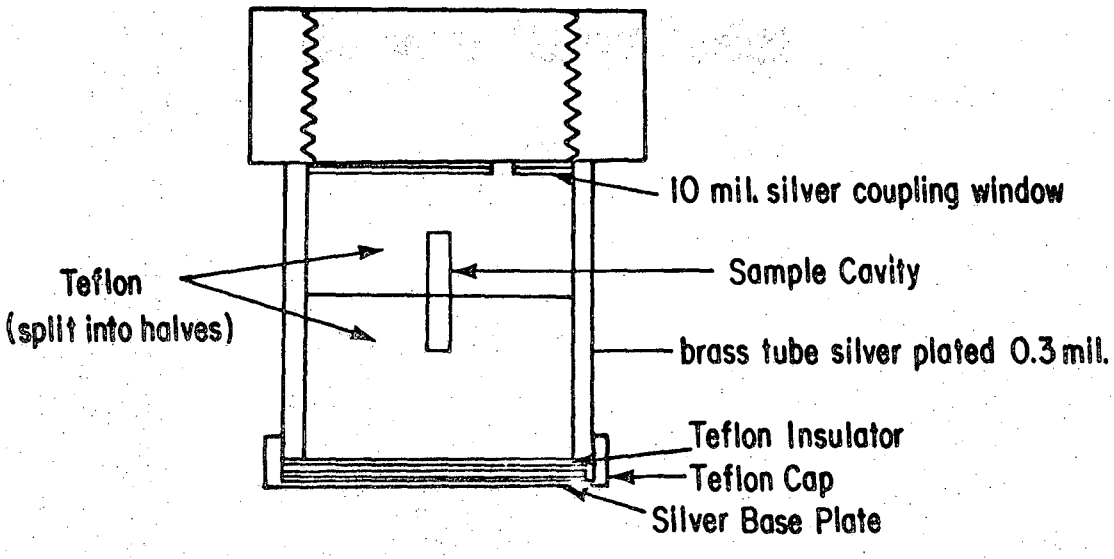
Figure 1



Absorption Spectrometer

XBL 703-469

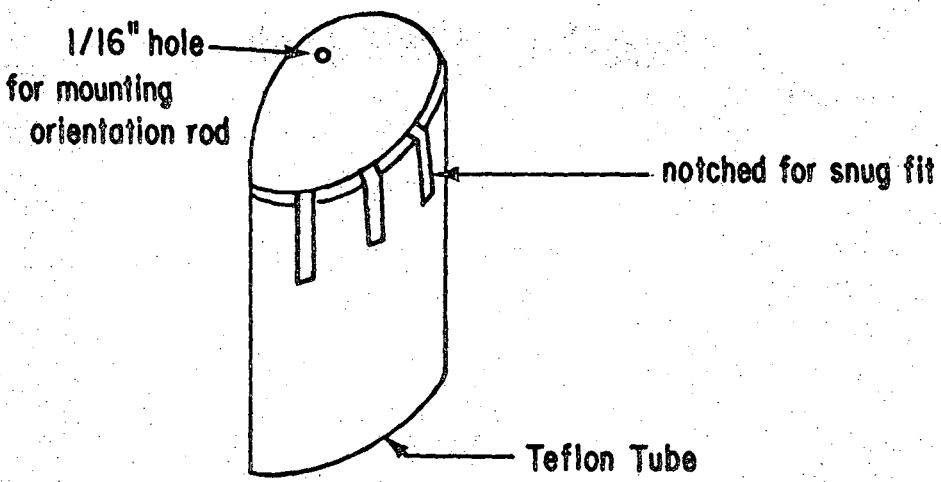
Figure 2



Resonant Cavity Design

XBL 703-470

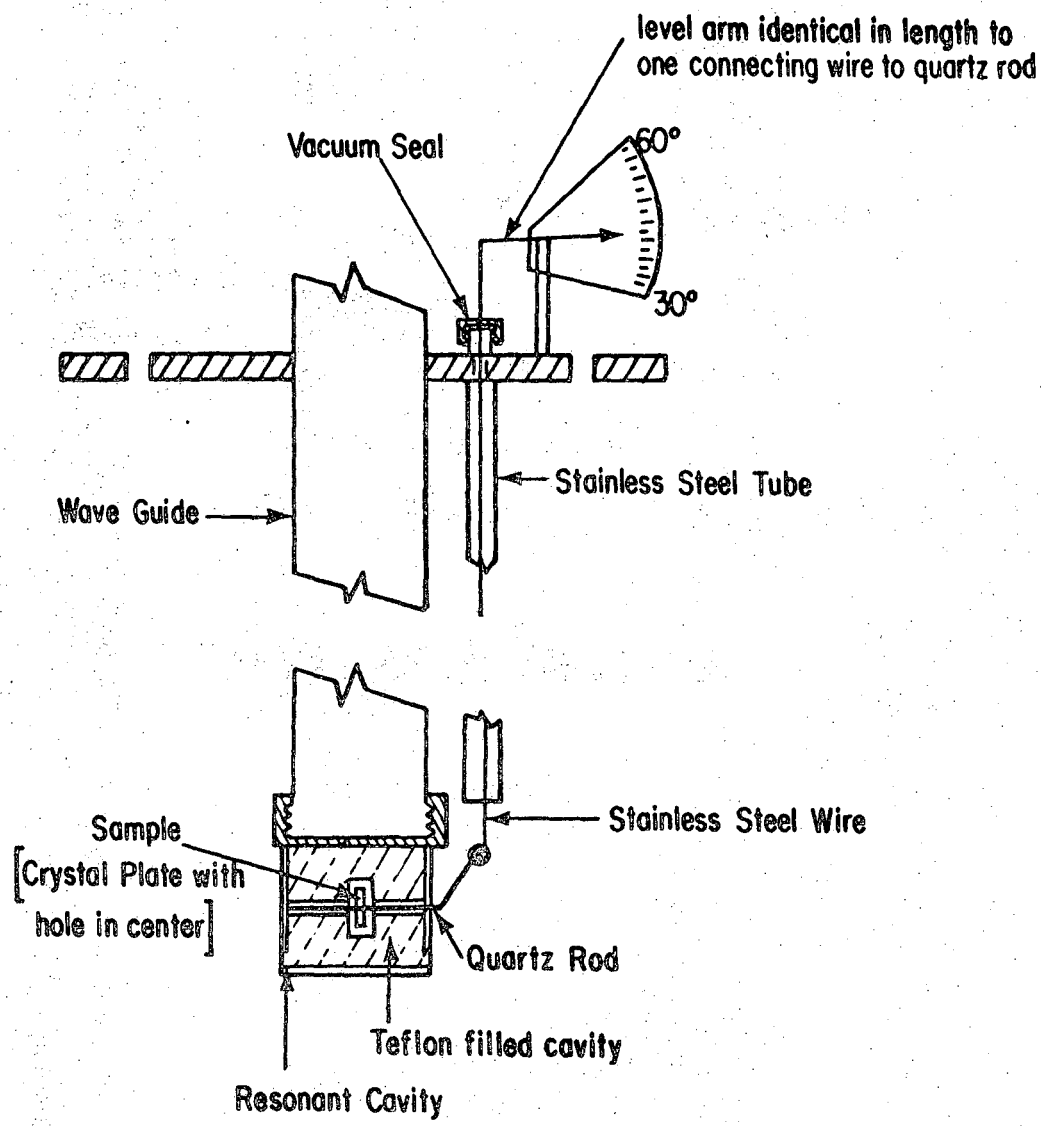
Figure 3



Spherical Ball Mount

XBL 703-471

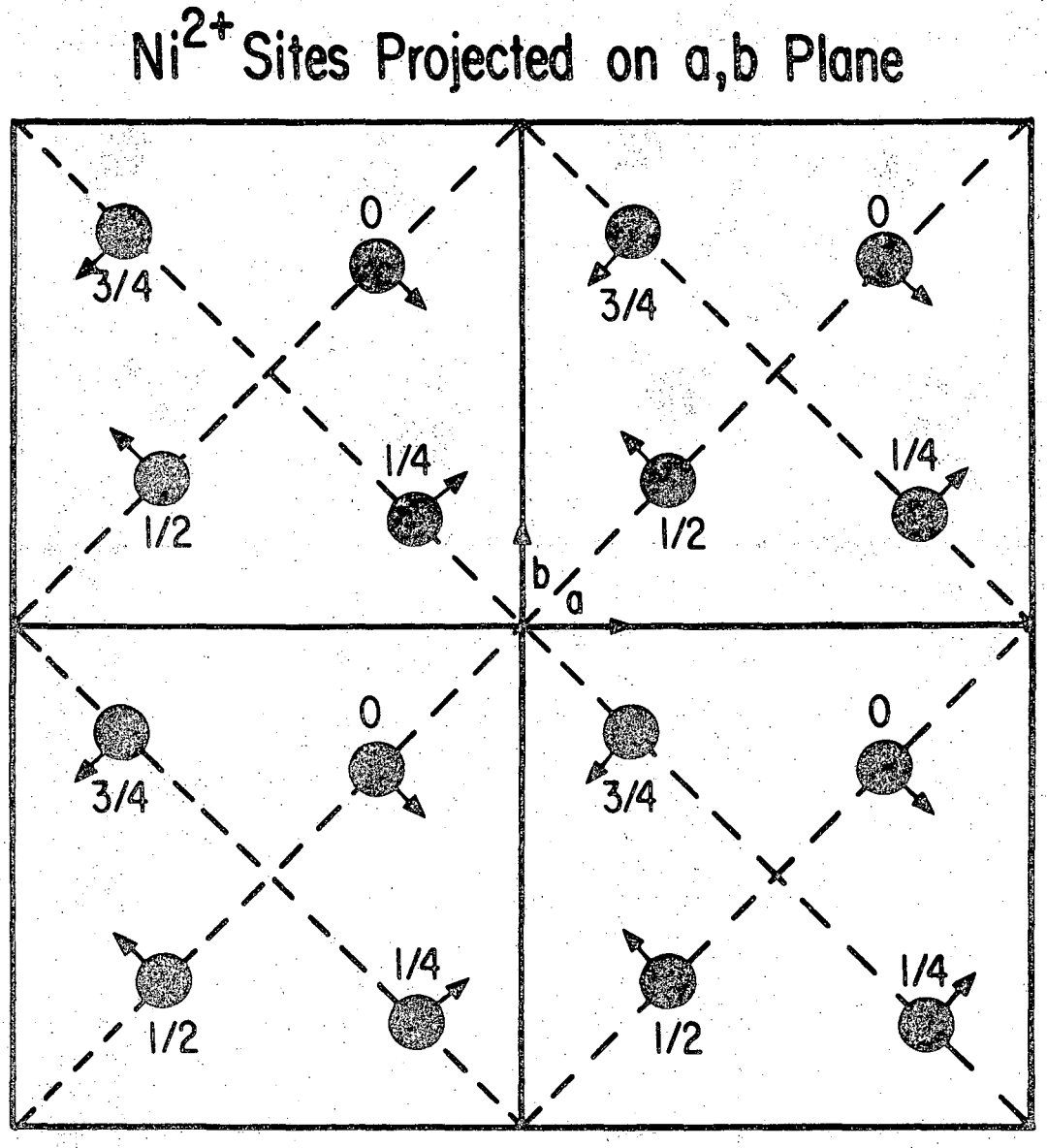
Figure 4



Crystal Rotator Apparatus

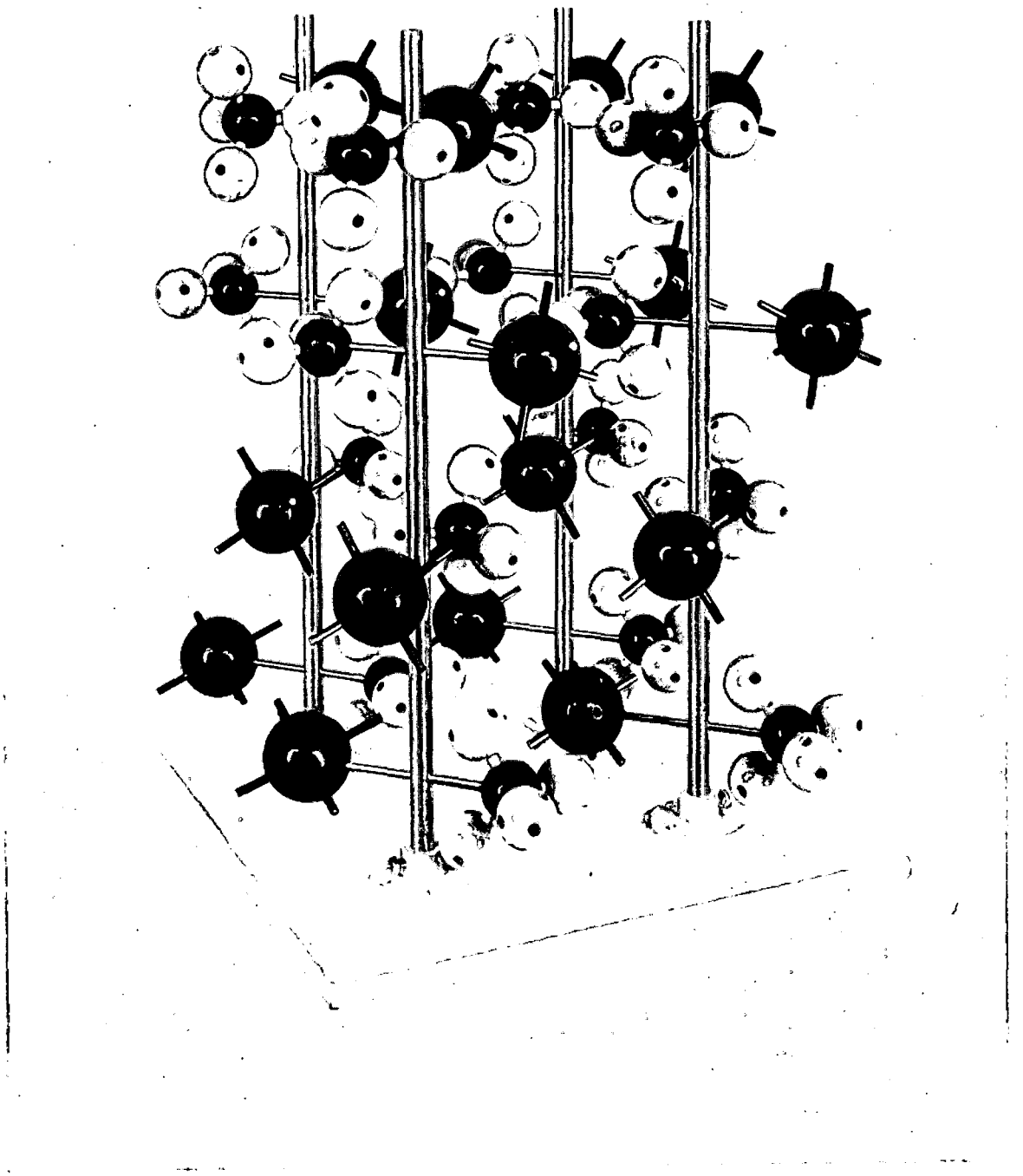
XBL 703-472

Figure 5



XBL 703-473

Figure 6



CBB6910-6530

Figure 7

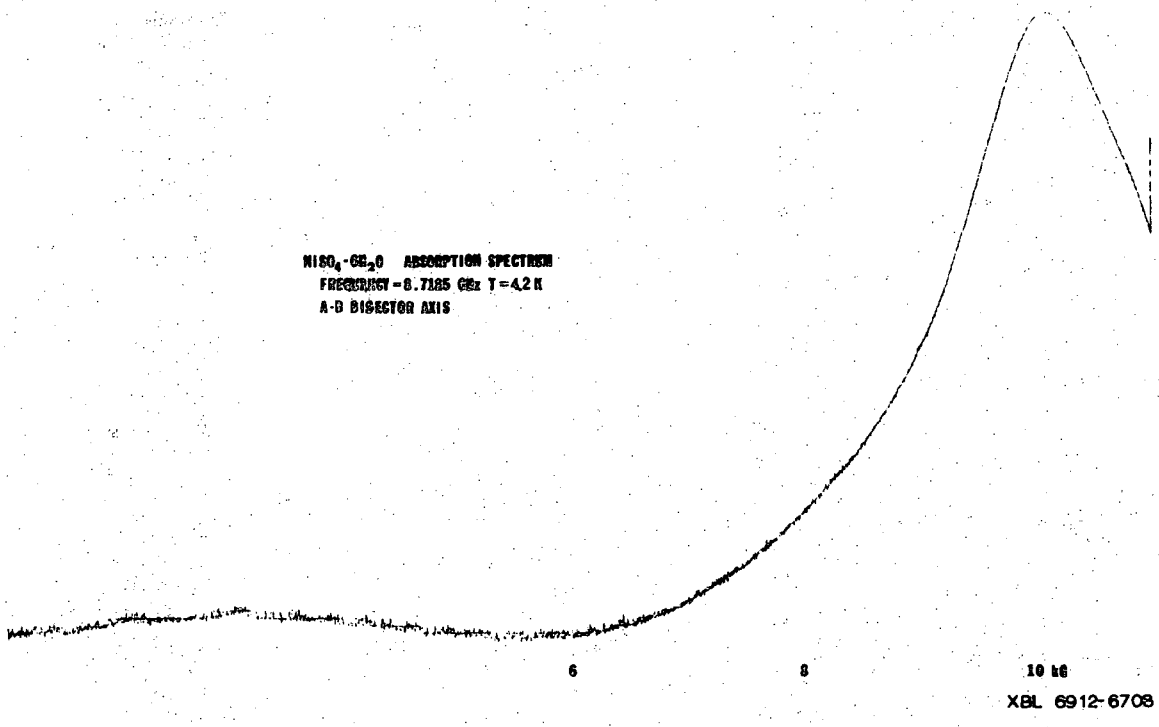

$NiSO_4 \cdot 6H_2O$ ABSORPTION SPECTRUM
FREQUENCY = 8.7185 GHz T = 4.2 K
A-B BISECTOR AXIS
6
8
10 kG
XBL 6912-6708

Figure 8

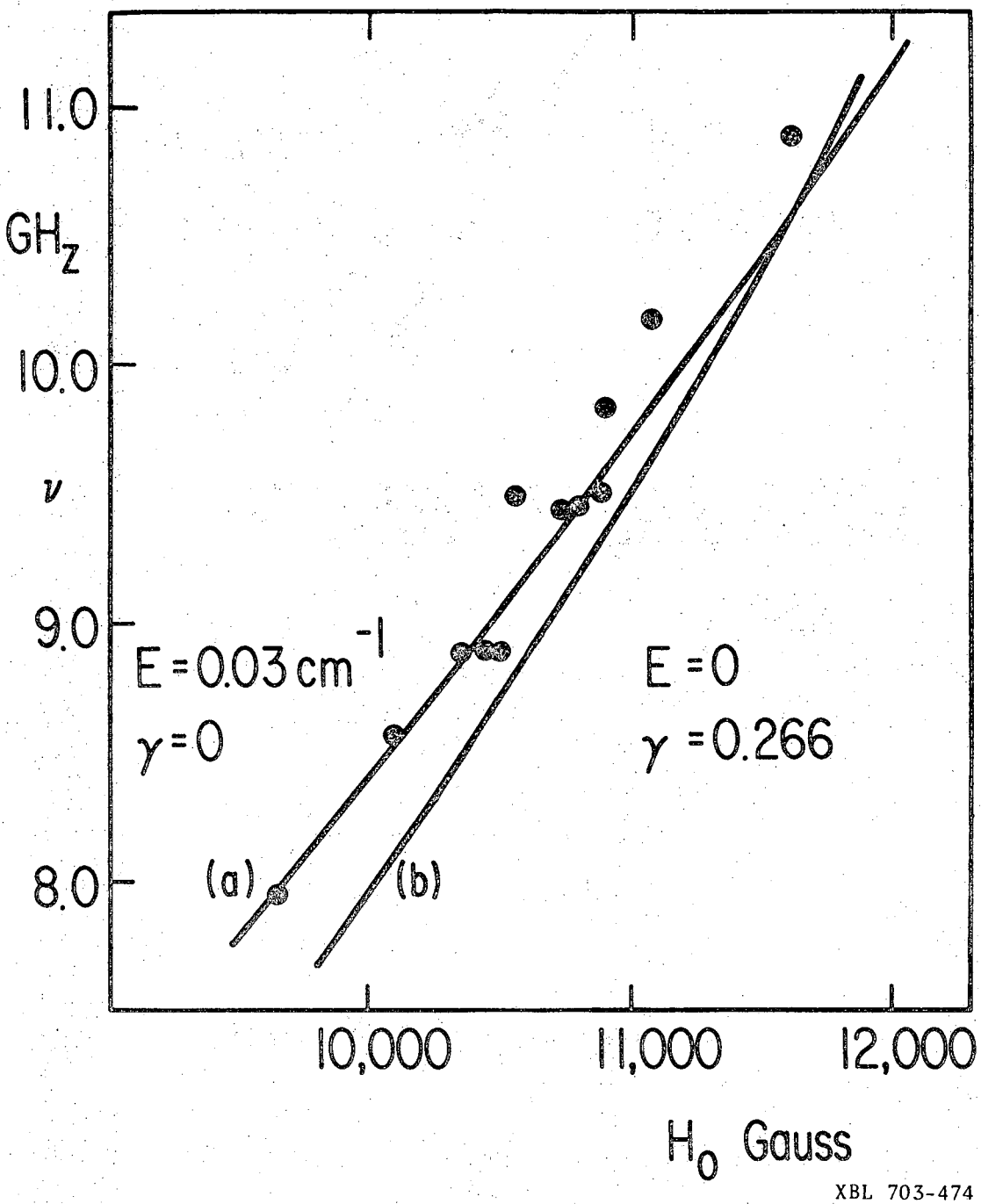
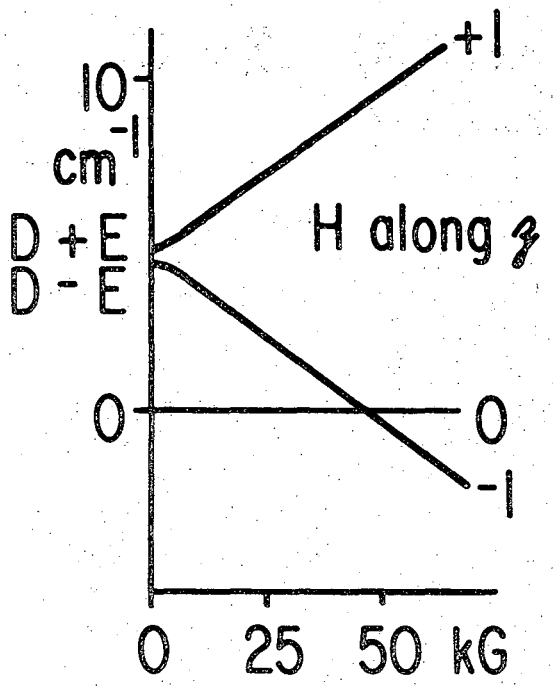
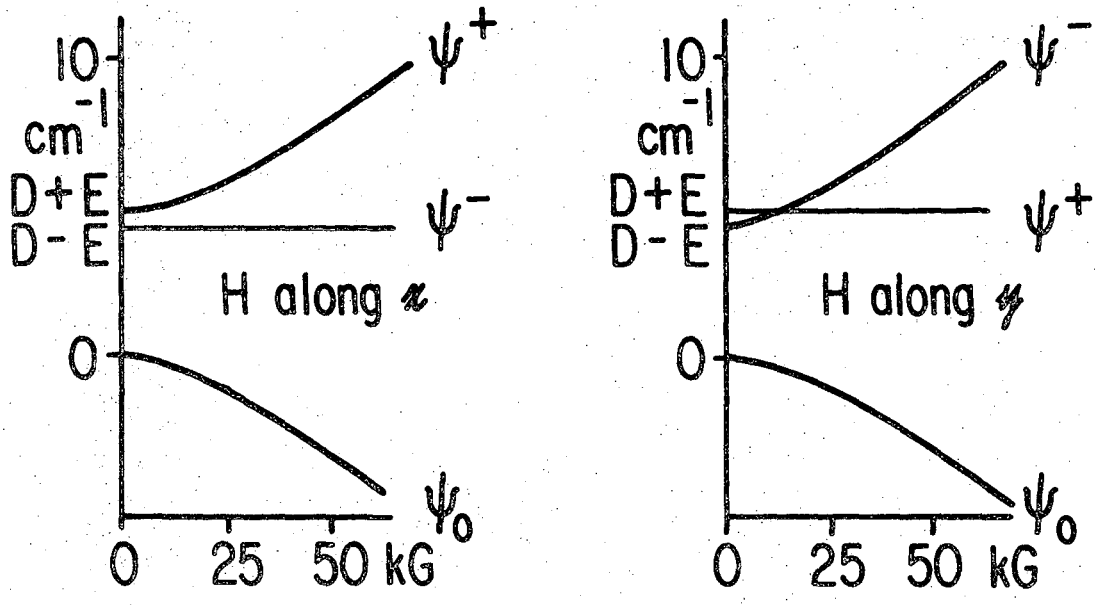

11.0
GHz
10.0
ν
9.0
8.0
E = 0.03 cm⁻¹
γ = 0
E = 0
γ = 0.266
(a)
(b)
10,000
11,000
12,000
H0 Gauss
XBL 703-474

Figure 9



XBL 703-475

Figure 10a



XBL 703-476

Figure 10b and c

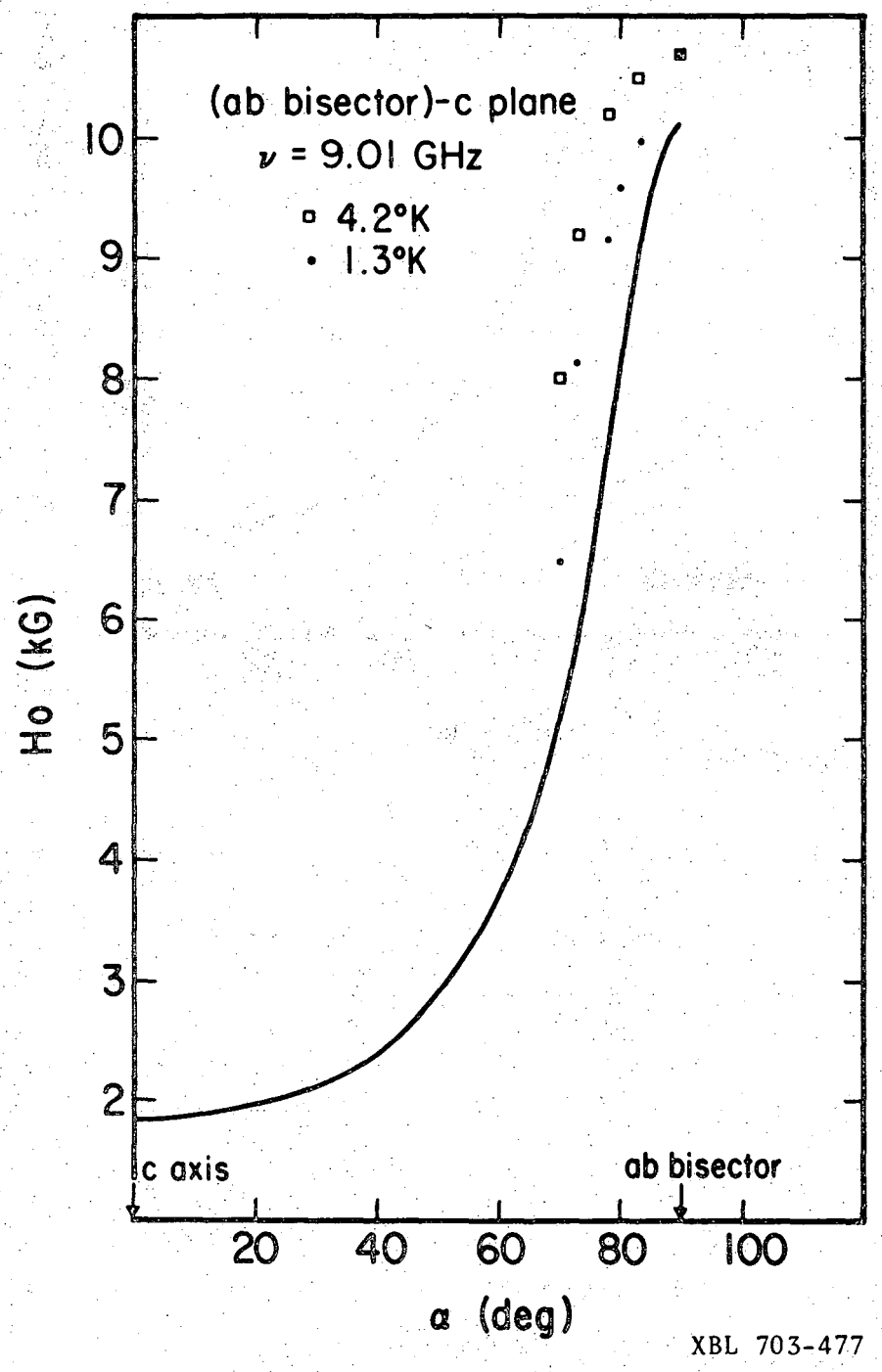

(ab bisector)-c plane
ν = 9.01 GHz
4.2°K
1.3°K
Ho (kG)
10
9
8
7
6
5
4
3
2
c axis
ab bisector
20
40
60
80
100
α (deg)
XBL 703-477

Figure 11

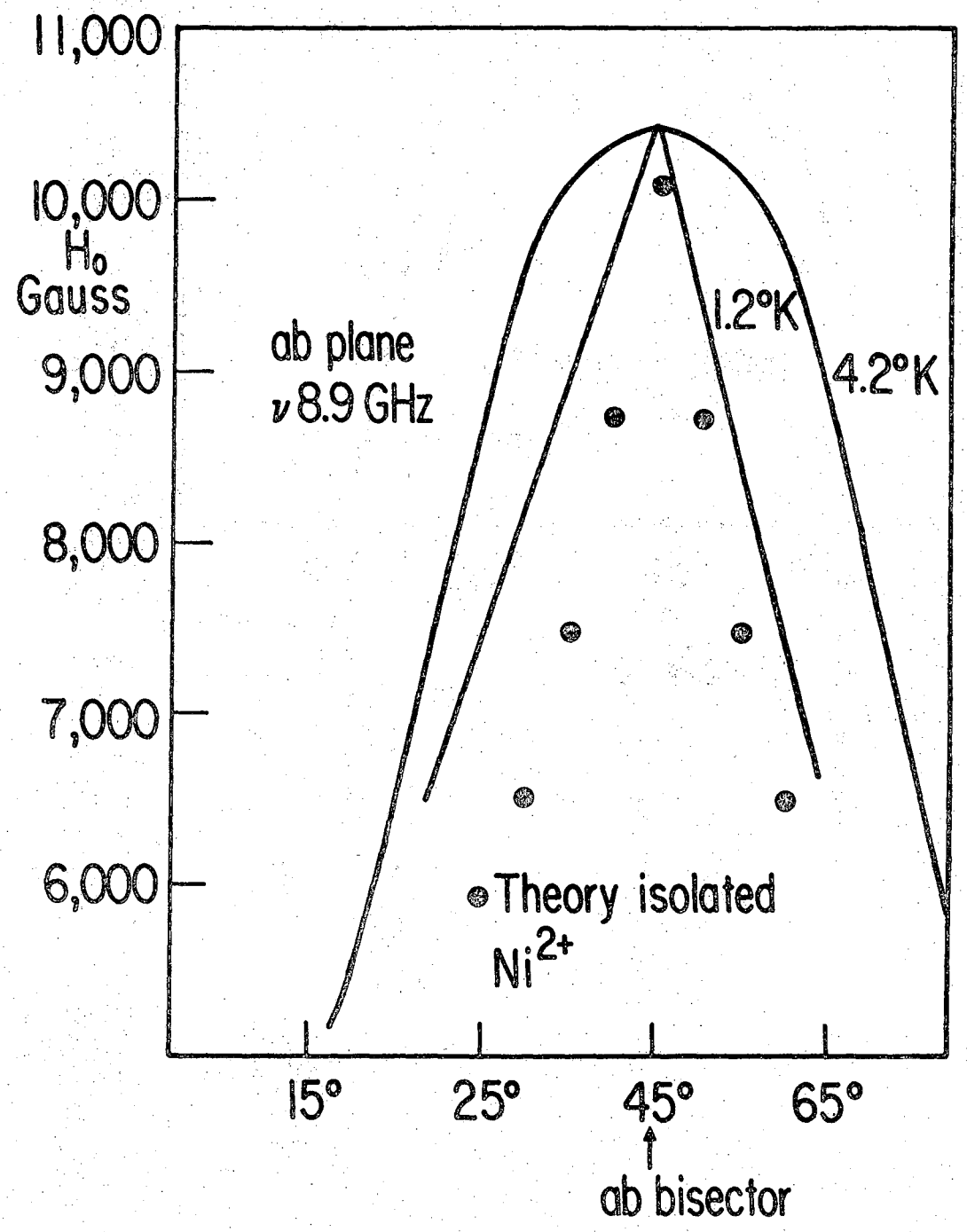
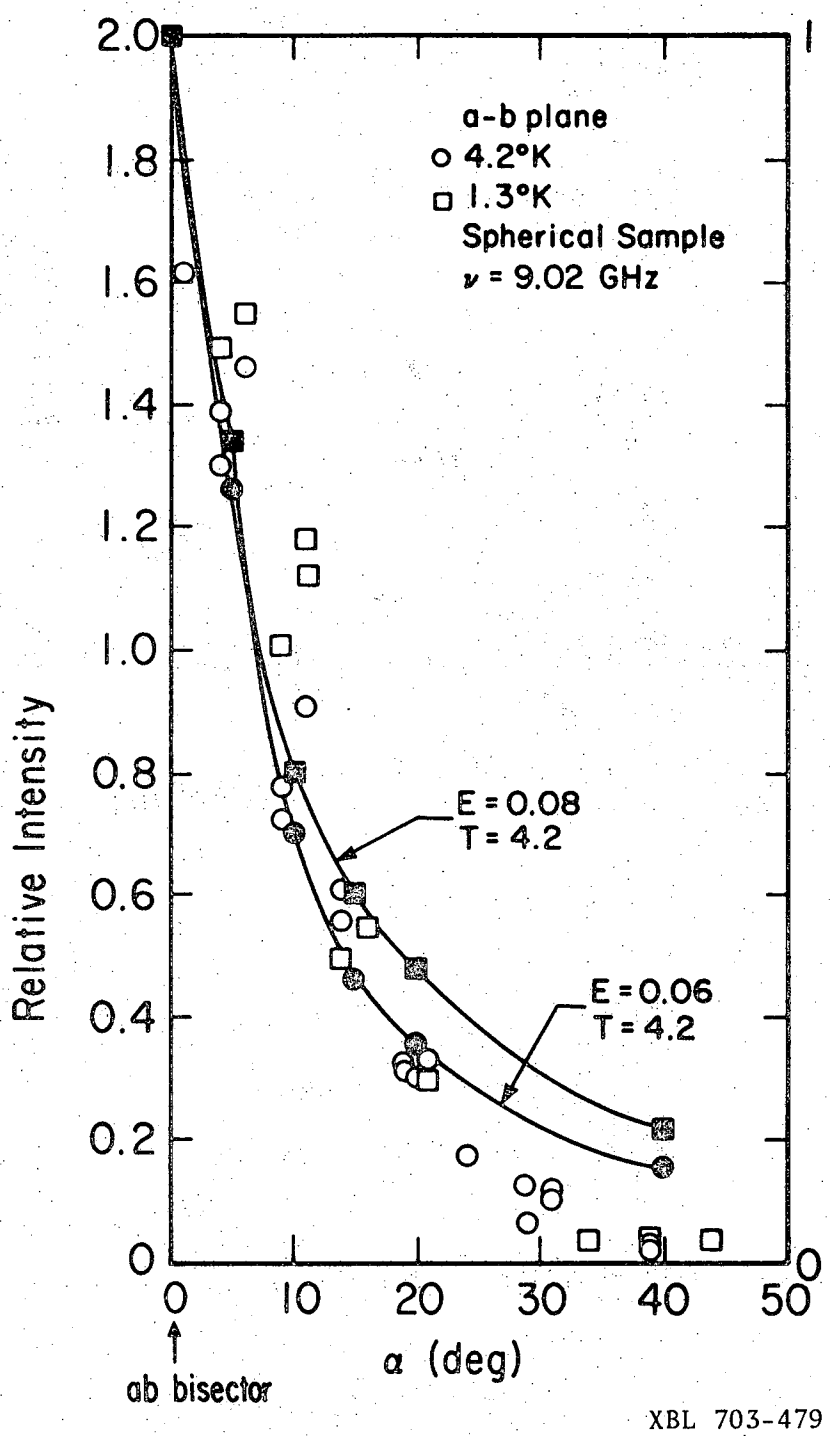
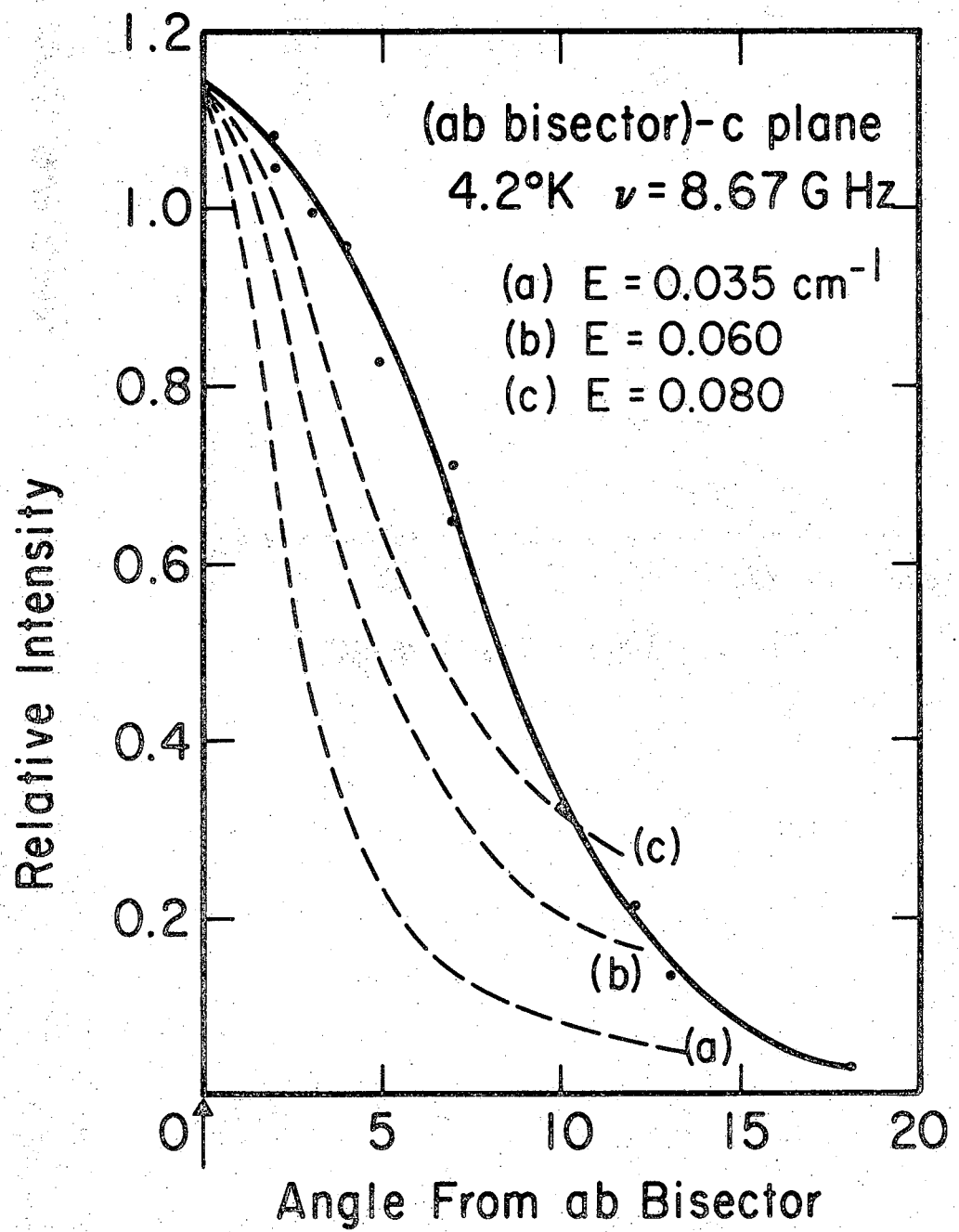

11,000
10,000
H_o
Gauss
9,000
8,000
7,000
6,000
ab plane
ν 8.9 GHz
1.2°K
4.2°K
Theory isolated
Ni^{2+}
15°
25°
45°
65°
ab bisector
XBL 703-478

Figure 12



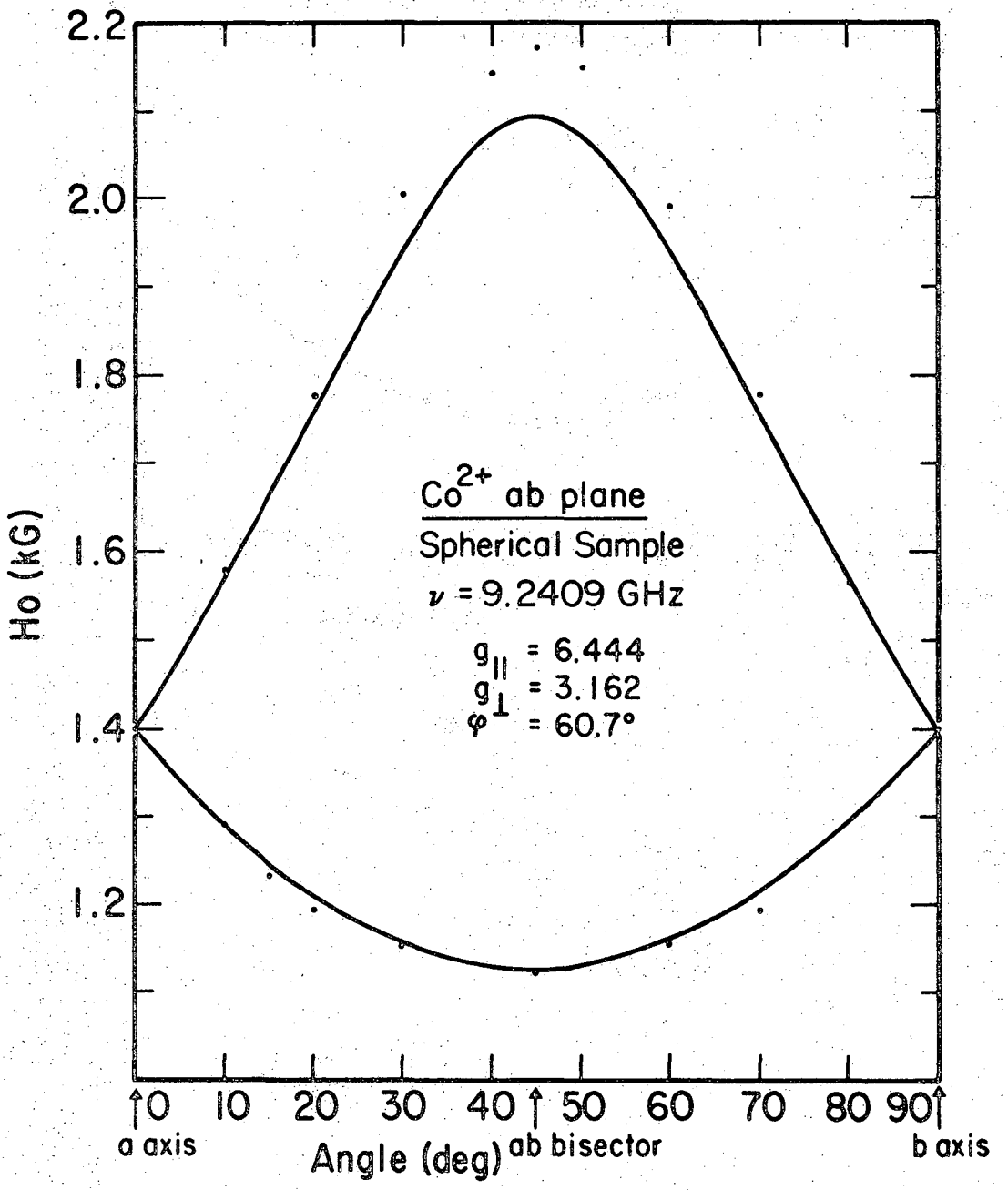
XBL 703-479

Figure 13



XBL 703-480

Figure 14



XBL 703-481

Figure 15

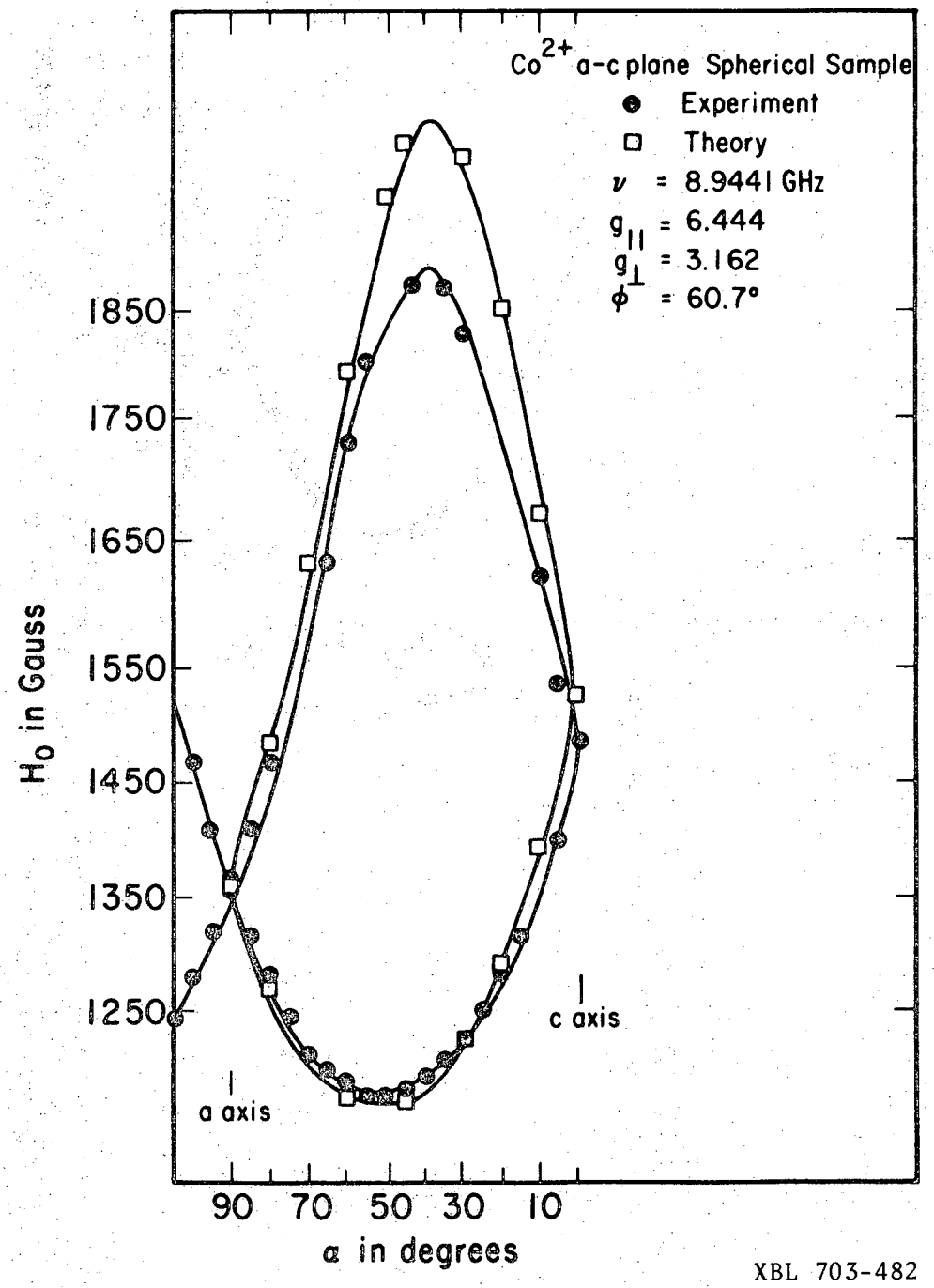
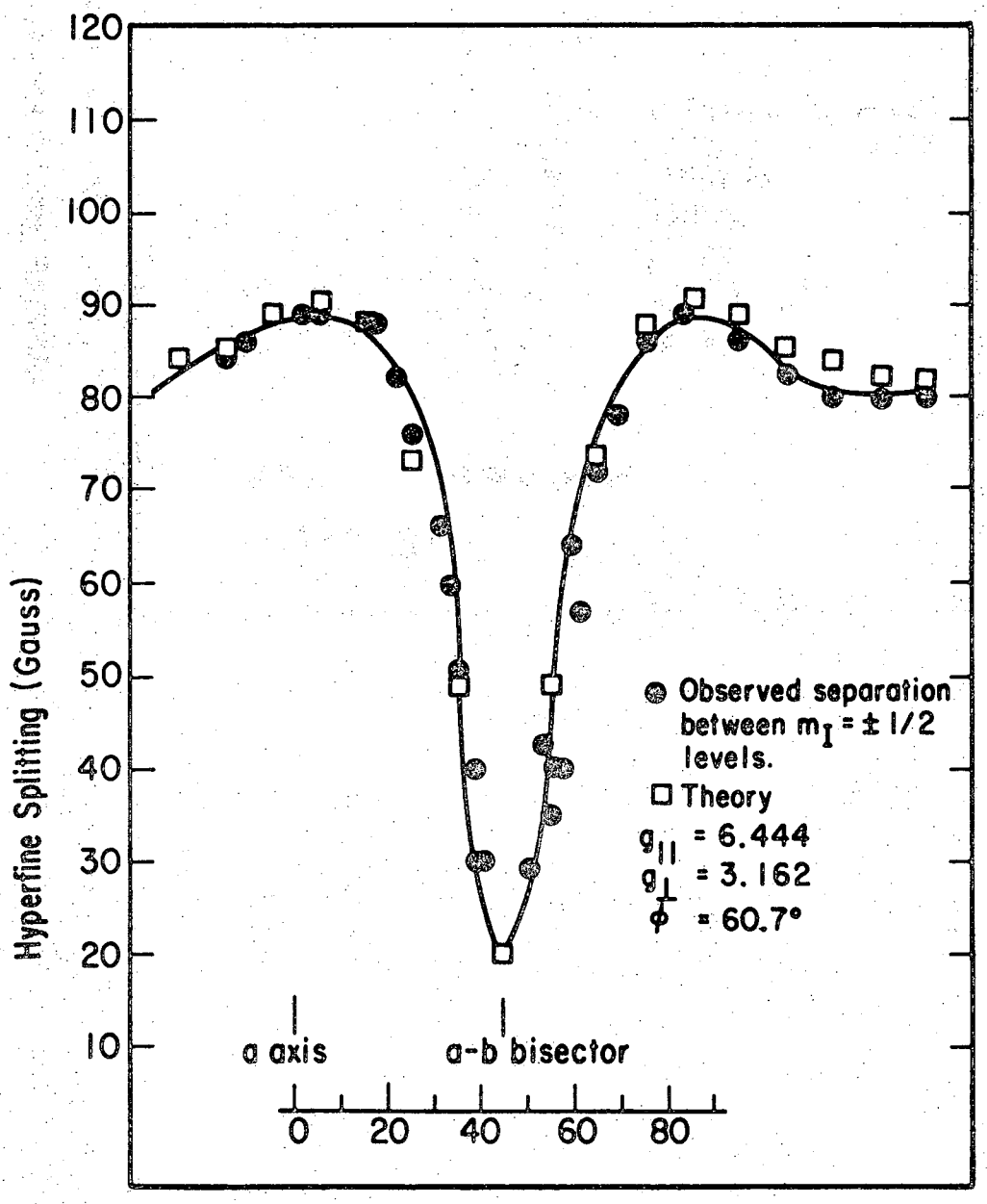

Co^{2+} a-c plane Spherical Sample
Experiment
Theory
ν = 8.9441 GHz
$g_{\parallel}$ = 6.444
$g_{\perp}$ = 3.162
ϕ = 60.7°
1850
1750
1650
1550
1450
1350
1250
H_o in Gauss
a axis
c axis
90 70 50 30 10
α in degrees
XBL 703-482

Figure 16



XBL 703-483

Figure 17

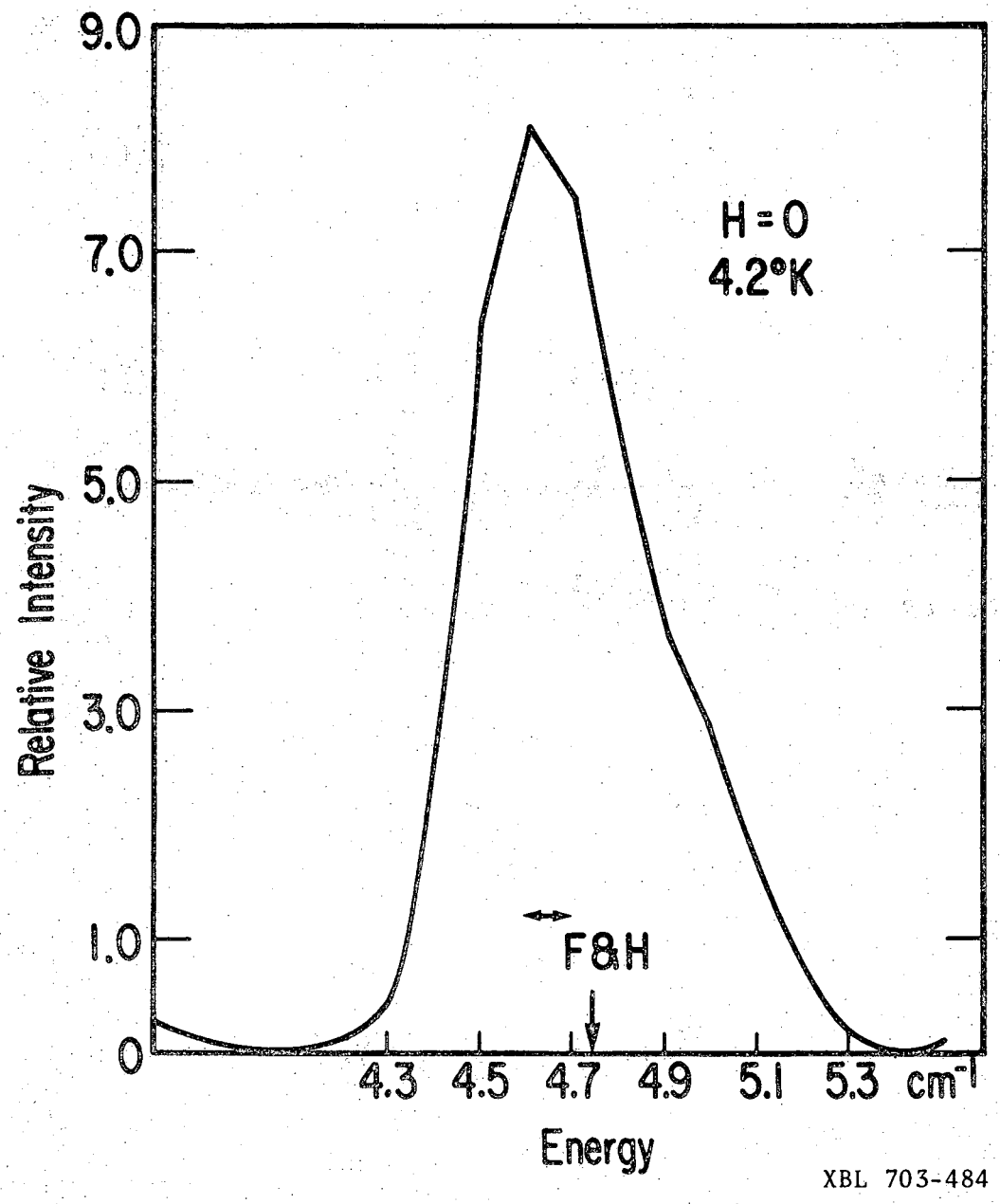

9.0
7.0
5.0
3.0
1.0
0
Relative Intensity
H=0
4.2°K
F&H
4.3
4.5
4.7
4.9
5.1
5.3
cm⁻¹
Energy
XBL 703-484

Figure 18

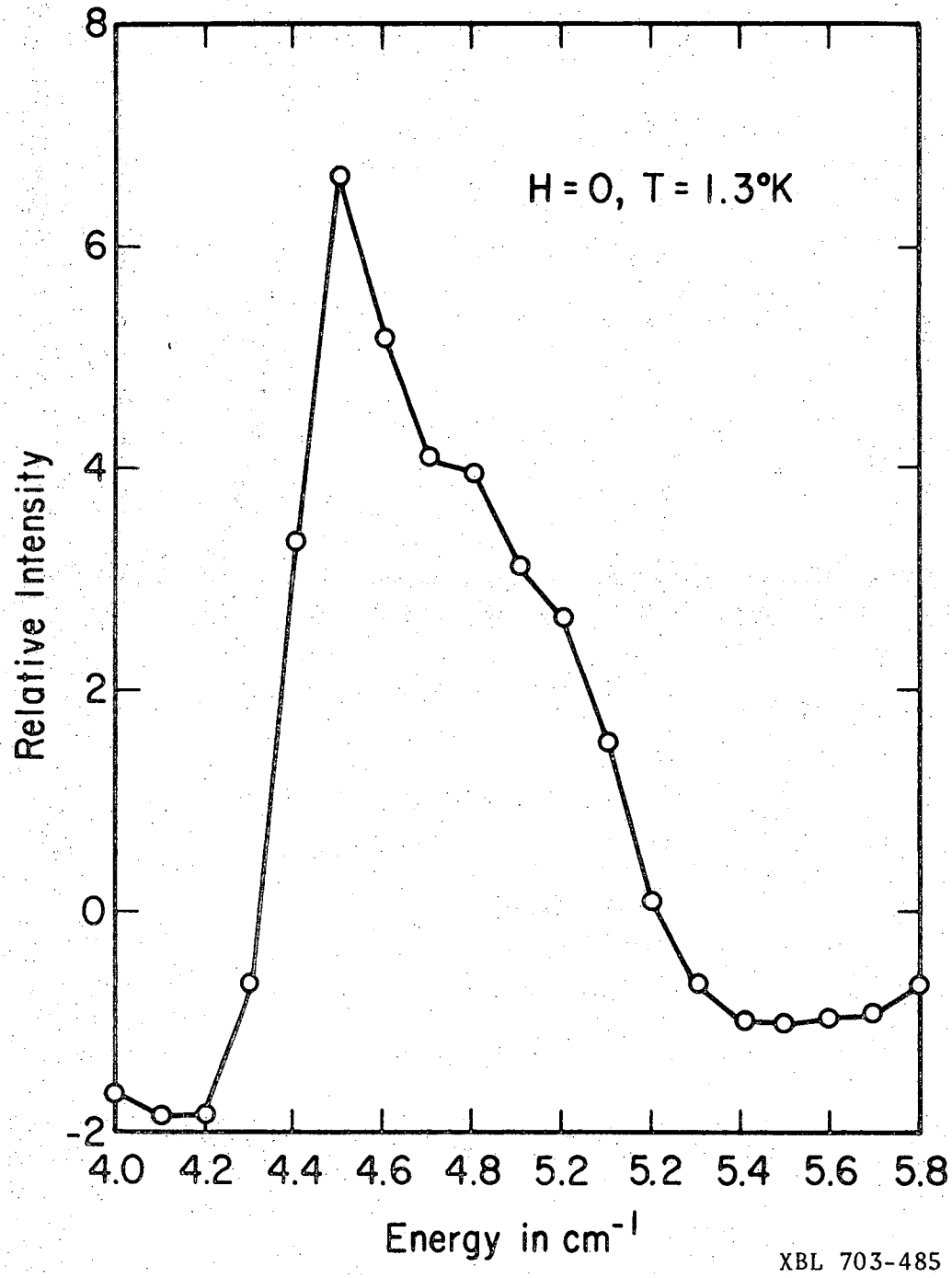

H = 0, T = 1.3°K
Relative Intensity
8
6
4
2
0
-2
4.0
4.2
4.4
4.6
4.8
5.2
5.2
5.4
5.6
5.8
Energy in cm⁻¹
XBL 703-485

Figure 19

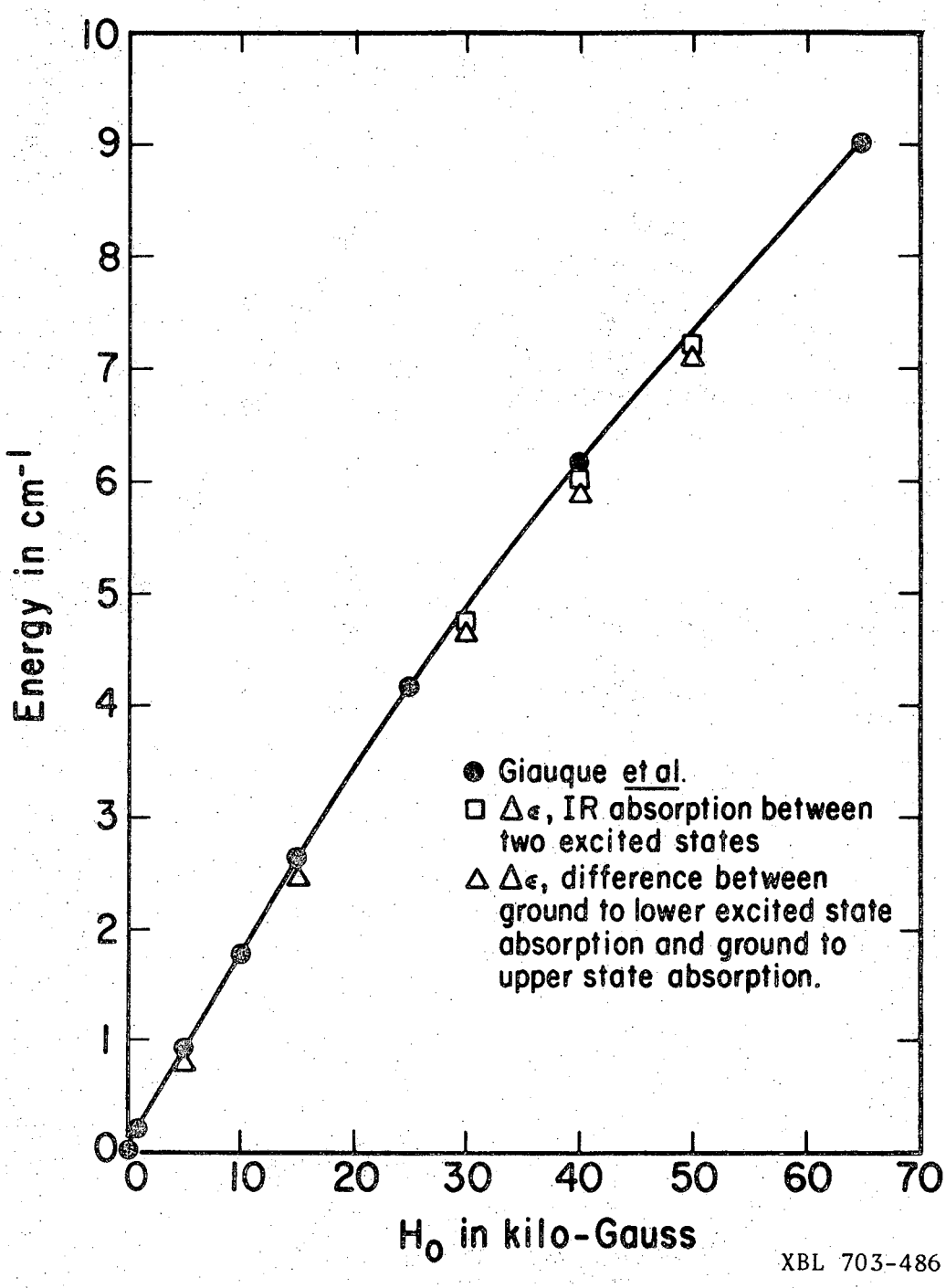

Energy in cm⁻¹
H₀ in kilo-Gauss
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
Giauque et al.
Δε, IR absorption between two excited states
Δε, difference between ground to lower excited state absorption and ground to upper state absorption.
XBL 703-486

Figure 20

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