Title
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Publication Date
1963

UCRL-10583

University of California

Ernest O. Lawrence Radiation Laboratory

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Berkeley, California

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Submitted to Physical Review for publication

UCRL-10583

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

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ABSTRACT

Mössbauer resonance experiments were performed on europium metal, using the 21.7 kev gamma ray in Eu^{151}. The Néel point of $87^{\circ}K$ was confirmed. Above this temperature a single line was observed and attributed to paramagnetic relaxation. At $4.2^{\circ}K$ a six-line spectrum was found. Analysis yielded a spin of 7/2 and a moment of + 2.53 ± 0.03 nm. for the 21.7 kev excited state, an internal field of 264 ± 8 kgauss, and an isomeric chemical shift of − 0.81 ± 0.03 cm/sec, relative to Eu_2O_3. This is consistent with an electronic level $4f^7 6s^2, {}^8S_{7/2}$ for the europium atom. The effect of nuclear deformation on isomeric chemical shifts is considered, and it is concluded that Eu^{151}, with a moderately deformed ground state, has a less deformed excited state at 21.7 kev.

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I. INTRODUCTION

Experimental determination of hyperfine magnetic fields in metals has become an important factor in elucidating the mechanisms of ferromagetism. The requirement that they reproduce the magnitude and sign of the observed magnetic field at the nucleus is a sensitive and stringent test of electronic wave functions associated with magnetic behavior. None of the available experimental methods (NMR, Mössbauer absorption, heat capacity measurements, nuclear orientation, and angular correlations) are really generally applicable, and they share the common fault of failing completely in certain situations. Still, enough workable cases have been found to provide data on about twenty hyperfine fields, and indeed these cases are sufficiently representative that one may begin now to speak of "trends".

Europium exhibits magnetic behavior, becoming antiferromagnetic at $87^{\circ}K$ [1] and possibly ferromagnetic at lower temperatures. It is one of the more interesting of the rare earths because the atomic level is presumably $4f^{7}6s^{2}$; $^{8}S_{7/2}$, and the hyperfine field, as in other half-filled shells, has more complex origins than simply the orbital angular momentum of the unperturbed lowest level. Moreover, neutron diffraction data indicate that europium has a spiral antiferromagnetic structure.[1]

We have observed hyperfine structure in europium by means of Mössbauer absorption experiments on Eu^{151}. Several spectra were taken near

the Néel point to delineate the main features of the temperature dependence there, but no systematic study was made of the temperature range below 87°K, where collective magnetic behavior is observed. We have, rather, concentrated on characterizing the spectrum at 4.2°K, to derive the hyperfine field and nuclear moments.

II. EXPERIMENTAL

The apparatus will be described in detail elsewhere. It consists of a three-walled double-dewar system into which a "drive capsule" holding the source and absorber is inserted. The Doppler velocity is produced and detected by electromechanical transducers, also in the capsule. The source can be placed within a few cm. of the detector, and gamma rays pass through thin Mylar and beryllium windows. The inner dewar retains liquid helium for about 40 hours.

A source of Gd^{151} in a lattice of Eu_2O_3 (enriched in Eu^{153}) provided a single line for this work. The Eu^{+3} ion has a $^7F_0$ level lowest; consequently there is no hyperfine structure in first approximation.[2,3] The 21.7 kev γ ray has a mean life of $\sim 10^{-8}$ sec. and a recoil-free fraction in this source of at least 0.36 at room temperature.[4]

Europium is chemically the least stable of the rare earth metals. It is violently oxidized by water and decomposes to a yellow oxide in a few minutes if left unprotected in the air. The absorbers used in this work were rolled (to 0.002 inches) and cut under kerosene, rinsed in ether, and immediately sealed in a sandwich of 0.001-inch Mylar tape. When not in use, they were stored at 77°K.

III. RESULTS

Europium is one of the "softest" rare earth metals in many ways, with anomalously low transition points,[5] and one might estimate its Debye temperature to be no more than 140° at most. Although it was not possible to derive Debye-Waller factors from this work, the magnitude of the absorption was consistent with a Debye temperature in this range. The highest temperature at which a spectrum was taken was 100°K. As this is well above the Néel point, the hyperfine field might be expected to be averaged to zero by paramagnetic relaxation, producing a single-line spectrum. Indeed only one line was observed, at a relative velocity of -0.82 ± 0.05 cm/sec.[6] Thus the nuclear level spacing for the isomer and the ground state of Eu^{151} is larger in Eu_2O_3 than in Eu metal. All the lower-temperature points were also shifted by ~ -0.8 cm./sec., indicating that the magnetic transitions induced no gross change in the 6s (conduction) electron configuration.

Figure 1 shows the isomeric levels of Eu^{151}. Data from several temperatures near the Néel point are shown in Figure 2. As the temperature was lowered to 77°K the line broadened to a complex but unresolved hfs pattern. At 100° the linewidth was 0.35 cm./sec., near the natural width (although the lifetime of the 21.7 kev state has not been determined directly, a lower limit of 9.2 nsec. has been set.[4] If we assume that any excess linewidth in the data of ref. 4 arises from unresolved hyperfine structure, we may set an upper limit of ~ 15 nsec. on the transition lifetime. Then the minimum possible experimental linewidth is in the range 0.14-0.23 cm./sec.). Thus the broadening with decreasing temperature may be associated with the onset of antiferromagnetism. The great difference between the absorption spectra at 86° and 90° (Fig. 2) provides confirmation of the

Néel point of 87°K and indicates that europium is paramagnetic at higher temperatures.

The magnetic behavior of europium below 87°K is apparently complicated and not well understood. Before Mössbauer experiments can be usefully applied to this problem, it is necessary to characterize the nuclear Zeeman spectrum. Thus an experiment was done at 4.2°K, where it was hoped that the hyperfine field would be large enough to resolve the pattern. The spectrum shown in Figure 3 was obtained. It consists of 4 equally spaced strong lines of equal intensity, centered around -0.81 ± 0.03 cm./sec., and two lines of about 1/4 this intensity with slightly greater spacing.

IV. NUCLEAR MOMENTS AND THE HYPERFINE FIELD

A hyperfine field can be derived from the spectrum at 4.2°K provided that the nuclear g-factor for each state is known. First we observe (Fig. 3) that there is no evidence for quadrupole splitting (i.e., the spectrum is completely symmetrical about -0.81 cm./sec.). Thus the positions of the hfs levels in either isomeric state are given by a Hamiltonian of the form AM_I. For a given set of nuclear spins and a given sign for the magnetic-moment ratio in the two isomeric states, the totality of all possible hyperfine spectra is given by a "g-factor diagram", an example of which is shown in Figure 4. The ordinate is the ratio of g-factors: its range is zero to infinity. The abcissa has dimensions of energy. The experimental spectrum of Eu^{151} falls on the horizontal line A-A. The relative positions of the Zeeman components on this line are exactly equal to their relative positions in the spectrum. The intensities also fit very well, as shown by the theoretical curve in Figure 3. The two very weak outside lines indicated on the diagram were not searched for. We note that

the experimental g-factor ratio falls at a remarkably fortunate value, allowing the four rather sharp central lines to absorb 88% of the transition intensity.

The ground-state spin and magnetic moment were known to be 5/2 and +3.419 nm.[7] The 21.7 kev transition is magnetic dipole.[8,9] Thus the excited-state spin had to be 3/2, 5/2, or 7/2. There was very good evidence from nuclear spectroscopy that the 7/2 choice was correct.[10] Indeed of the six possible combinations of excited-state spin and sign of the excited-state magnetic moment, only the 7/2,+ combination (Fig 4) fits the data, and this fits only position A-A, for which $g_1/g_o = +0.528 \pm 0.005$. Thus the excited-state spin is 7/2, and the magnetic moment is +2.53 ± 0.03 nm. The corresponding hyperfine field is 264 ± 8 kgauss.

It is customary to separate atoms in metals conceptually into ion cores and conduction electrons. In europium the electronic configuration is $4f^7 6s^2$, which is thought to produce a $4f^7$, $^8S_{7/2}$ ion core, with the two 6s electrons going into the conduction band. If the situation is really this simple and there are no effects such as conduction-electron polarization, the hyperfine field should be just that produced by the $^8S_{7/2}$ level. A calculation of this field from fundamentals is not straightforward, but a reasonable estimate may be obtained from EPR data on Eu^{+2}, which has the $^8S_{7/2}$ level lowest. Values of A_{151} in the Eu^{+2} spin-Hamiltonian range from 0.00308 to 0.00341 cm^{-1} for different environments,[11,12] indicating hyperfine fields between 311 and 343 kgauss. The agreement with this experiment is rather good, considering: 1. the sensitivity of the field at the nucleus to configuration mixing and conduction-electron polarization, 2. the approximate nature of the comparison, and 3. that the experiment was done at 4.2°K (this

was the bath temperature; the sample may have been a few tenths of a degree warmer) rather than absolute zero, and the field must be less than the saturation field. We thus interpret the hyperfine field as arising from the $^8S_{7/2}$ electronic level. Of course it is also possible that large core-polarization or conduction-electron polarization effects are present which change the sign of the net hyperfine field. This can be settled by determination of the sign. At present we can say that the magnitude of the field doesn't require such effects.

V. ISOMERIC CHEMICAL SHIFT AND NUCLEAR DEFORMATION

The chemical shift in Eu^{151} between the metal and the sesquioxide (i.e., between Eu^{o} and Eu^{+3}) is the second largest yet measured, the largest being in Au^{197}. In these two nuclei the large shift arises from a combination of 6s electron transfer plus unusual nuclear effects. In Au^{197} the nuclear effect is core excitation in the excited state;[13,14] in Eu^{151}, on the edge of the collective nuclear region,[3] the most plausible interpretation is that the excited state is less deformed than is the ground state.

The isomeric chemical shift is given approximately by the expression[15,16]

$$\delta E = \frac{2\pi}{5} Ze^2R^{2-2\rho}(\Delta\langle r^{2\rho}\rangle)(\Delta\psi(o)^2). \qquad (1)$$

Here R is the nuclear radius. The term in $\Delta\psi(o)^2$ for the Eu-Eu_2O_3 system is essentially twice the 6s electron density at the nucleus, because Eu has (in the conduction band) two 6s electrons which Eu^{+3} lacks. This electron density at the nucleus in the metal should be the same order of magnitude as that in the free atom, which is given by the expression[17]

$$\psi(o)^2 = \frac{1}{\pi a_o^2} \frac{Zi\ Z_a{}^2}{n_a{}^3} \left(1 - \frac{d\sigma}{dn}\right). \qquad (2)$$

There are not enough data available to obtain $\psi(o)^2$ for europium directly from experiment; instead we have interpolated this quantity, which should vary smoothly with Z, between atoms with alkali-like configurations, for which it may be determined directly.[17] This procedure gives

$$\psi(o)^2 = 5 \times 10^{25}\ \text{cm}^{-3} \qquad (3)$$

per 6s electron. From Eq. (1) and (3), with measured shift of 0.81 cm/sec, we obtain

$$\Delta\langle(\frac{r}{R})^{2\rho}\rangle = 0.0012, \qquad (4)$$

using $R = 1.2A^{1/3} = 6.4f$, with the ground state "larger" than the excited state. Because Eu^{151} is in a transition region there is no straightforward procedure available for explaining the observed value of $\Delta\langle r^{2\rho}\rangle$. Rather than presenting no explanation at all, we shall offer two possible, albeit crude, tentative interpretations. It should be clearly understood that these interpretations are speculative and are at best considerable over-simplifications of the problem. The procedure then is to approach the problem from the point of view of the two limiting cases, the nuclear shell model and the collective model.

The simple shell model can account for this size difference only by invoking "hole" states to give the observed sign. To make a shell model calculation, we assume (1) that the two states correspond to single holes in the $d_{5/2}$ and $g_{7/2}$ shells (holes are necessary to give the right sign), and (2) that the nuclear potential is a finite square well. With a nuclear radius of 6.4 f, we find, using the radial moments calculated by Eisinger and Jaccarino[18], $\Delta\langle r^2\rangle = 7.55f^2$ for the odd proton, or .12 f^2 for the entire nucleus. The quantity $\Delta\langle(\frac{r}{R})^2\rangle$ is thus 0.003. This is somewhat larger than the experimental value in Equation 4 (the two quantities are roughly comparable because the relativistic parameter, ρ, has the value 0.89, close to 1, for europium). Thus the single-particle shell model approach gives the right order of magnitude but the wrong sign, if we don't invoke "hole states".

Another possible explanation for the observed value of $\Delta\langle(\frac{r}{R})^{2\rho}\rangle$ may be obtained using the collective coordinates of the entire nucleus. Europium-151 is situated on the edge of the collective nuclear region, having an intrinsic deformation of $\delta = + 0.12$ in its ground state. This was calculated from the intrinsic quadrupole moment[3] of +2.66 barns, using the relation[19]

$$Q_o = \frac{4}{5}\,\delta Z R_o^{\,2}\,(\,1 + \delta/2 + \ldots). \qquad (5)$$

To calculate the effect of nuclear deformation on the isomeric shift, we may approximate a prolately-deformed nucleus by a uniformly charged ellipsoid bounded by the surface

$$R = R_o(1 + \alpha P_2(\cos\theta)\,) \qquad (6)$$

with $\alpha \gtrless 0$. The volume is equal to that of a sphere of radius $R_s = R_o(1-\alpha^2/4)$, to terms in α^2. For the ellipsoid the average-square radius is given by $\langle R^2 \rangle = R_o^2(1 + \alpha^2/2)$, again to order α^2. Thus in going from a spherical to an ellipsoidal shape a nucleus experiences a change in its second radial charge moment of $\alpha^2 R_s^2$, where R_s is the radius of the spherical nucleus, as defined above. Comparison with Eq. (1) yields an isomeric shift of

$$\delta E = \frac{2\pi}{5} Ze^2 \Delta \psi(o)^2 R_s^2 \Delta(\alpha^2). \qquad (7)$$

in nonrelativistic approximation, accompanying a change in nuclear deformation between the isomeric states.

Equation (7) has a very simple physical interpretation, and should be adequate for most situations, including the case of Eu^{151}. In particular we note that, by combining Eqs. (5) and (7), together with the well-known relation between the spectroscopic and intrinsic quadrupole moments[20] (and noting that our α is $\frac{2}{3}\delta$), one can derive explicit expressions relating the isomeric shift to either the quadrupole moments or to the deformations of the two states. In some cases (i.e., for very heavy nuclei) the non-relativistic approximation may not be suffiecently accurate. It may then be profitable to use the results of Wilets, Hill, and Ford,[21] who have considered the effect of nuclear deformation on isotope shifts in optical spectra in much more general terms. Lardinois[22] has applied these results to optical isomeric shifts. In our notation the isomeric shift in a Mössbauer resonance spectrum becomes

$$\delta E = \frac{2\pi}{5} Ze^2 \frac{3}{2\rho+1} R_s^2 \Delta\left[\sum \psi(o)^2\right] \Delta \left\{\alpha^2 \left[1 + \frac{2}{21}(2\rho + 3)\alpha + \ldots\right]\right\} \qquad (8)$$

We write the electron density term as a sum to emphasize that for heavy nuclei (high Z) one must consider all electrons which have a finite density at the nucleus, including the s-like small component of relativistic $\mathbb{P}_{1/2}$ electrons. As ρ approaches unity Eq. (8) reduces to Eq. (7) to order α^2, as it should.

From the above discussion we find $\Delta(\alpha^2) = 0.0011$ for Eu^{151}, with the ground state more deformed than the excited state. The intrinsic deformation of $\delta_o = +0.12$ corresponds to an α_o of +0.08. Thus $\alpha_1 = +0.07$ on this model. It is interesting to attempt an explanation for the decrease of deformation in one of the isomeric levels. This nucleus must be very delicately balanced with respect to deformation, and it seems unlikely that an unequivocal explanation can be given without first considering the theoretical situation very carefully. Perhaps the slightly larger increase with deformation of the energy of the 7/2+(404) Nilsson orbital[19] over that of the 5/2+(402) orbital can account for this result. Again a $d_{5/2}$ orbital is much smaller than a $g_{7/2}$ orbital, and it may be able to participate more in collective motions of the nucleus, including deformation.

It is most probable that the true explanation lies between these two extremes. In fact it seems likely that the two effects (single particle and collective) might compete, since the single particle calculation alone gives the wrong sign, with the collective effects being slightly stronger. Thus for example the difference in deformation may even be greater (perhaps the excited state is undeformed), with much of this effect on $\langle r^{2\rho} \rangle$ being cancelled out by the effect of the single-particle $g_{7/2}$ state.

Again we emphasize that this interpretation involves rather substantial approximations, including that of the 6s electron density in europium metal. On the nuclear side it should be realized that, while the

single

simple deformation picture is probably the best that can be used at present, Eu^{151} is in a transition region where no simple model is clearly applicable and a firm interpretation of the shift must be postponed until this transition region can be better understood.

FOOTNOTES AND REFERENCES

* Work supported by the United States Atomic Energy Commission.

**Summer visitor from the Department of Physics, University of California at Santa Barbara. Address until June, 1963: Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts.

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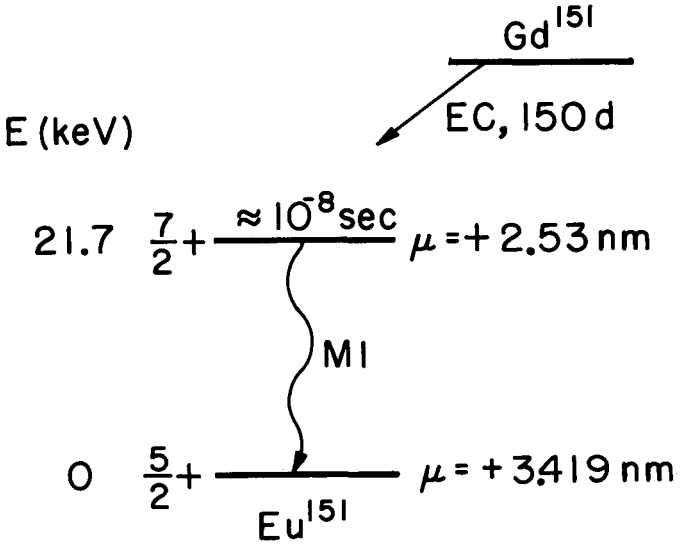


Fig. 1. The isomeric levels of Eu^{151} discussed in this paper.

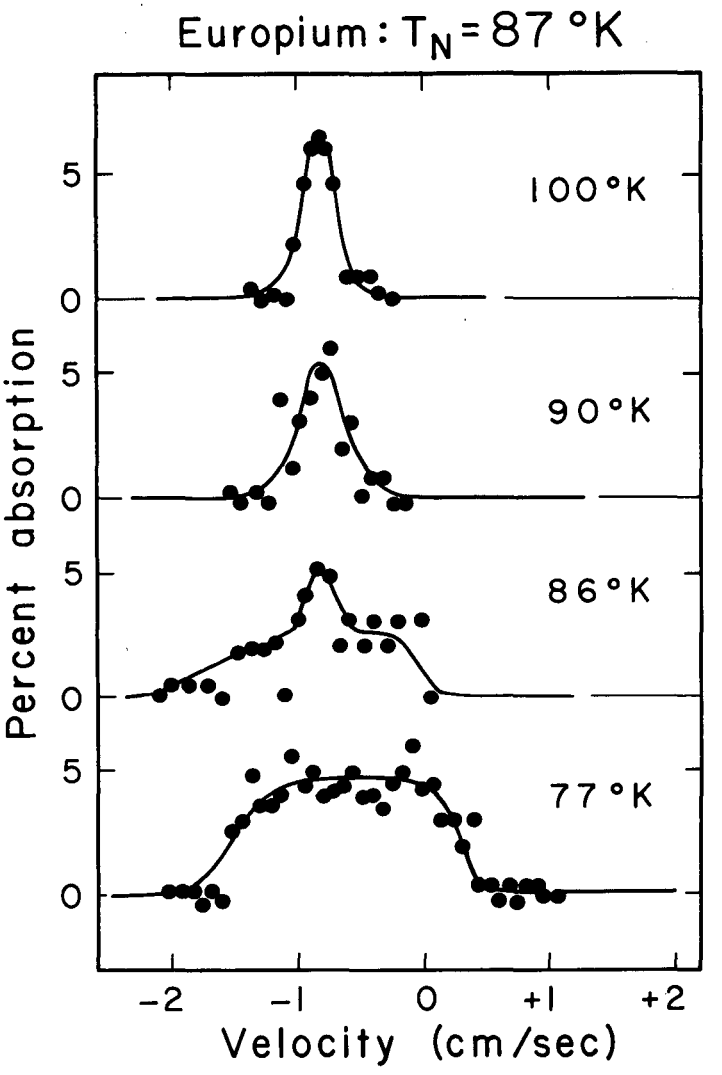


Fig. 2. The resonant absorption spectra of Eu^{151} in europium metal at several temperatures near the Néel point of 87°K.

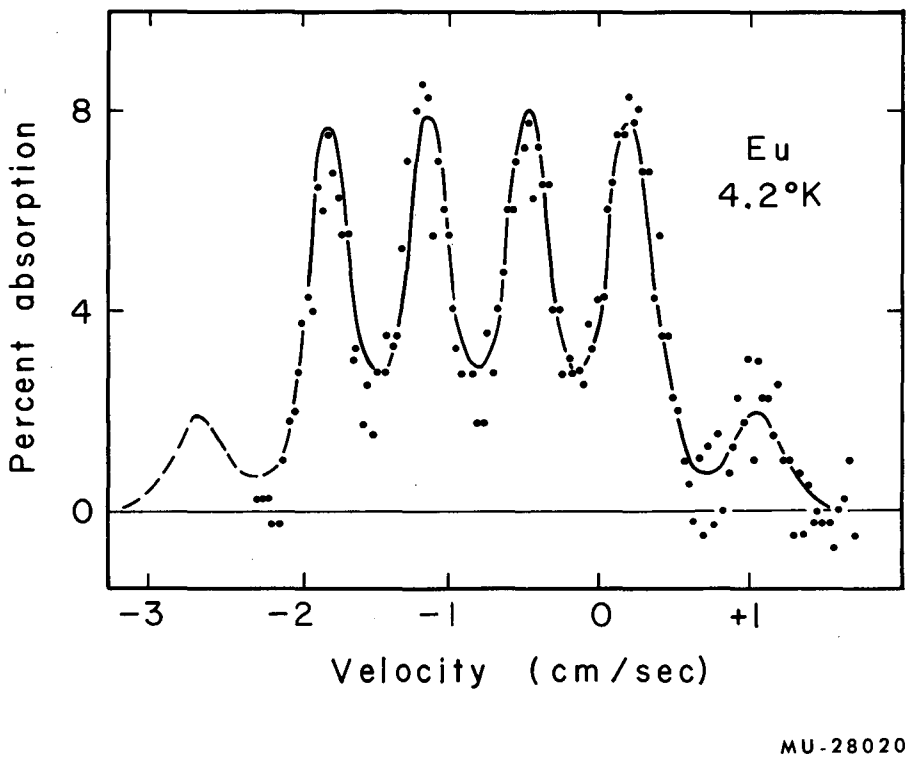
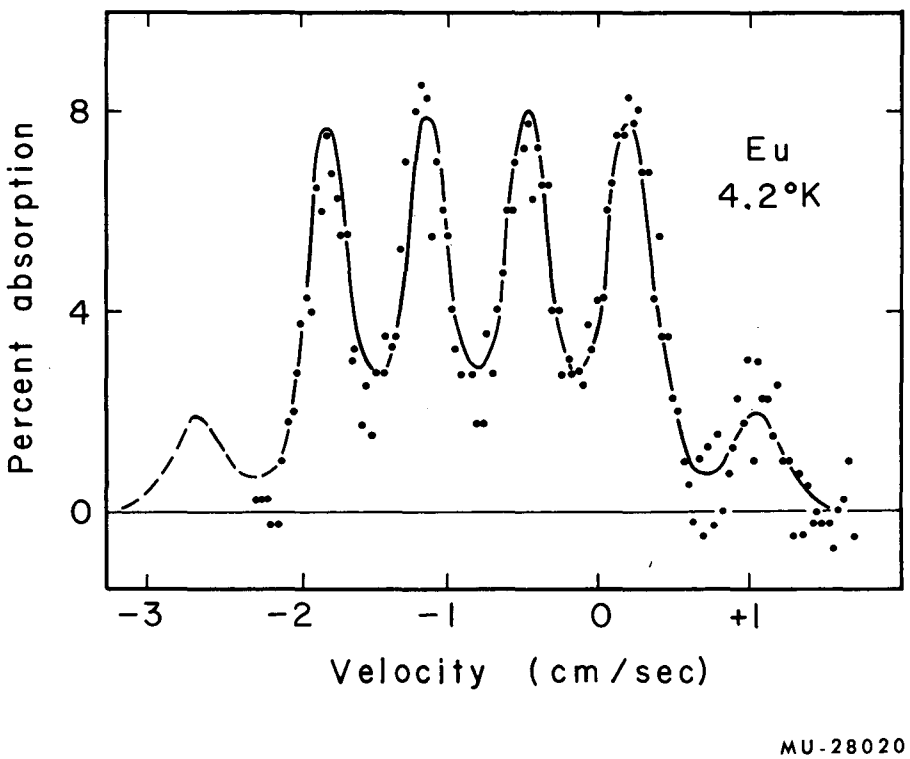


Fig. 3. The resonant absorption spectrum of Eu^{151} in europium metal at 4.2°K. The sweep did not go to high enough velocities to detect the weak line at −2.6 cm/sec in this run. In other runs this line was observed. The theoretical curve is for a g-factor ratio of + 0.528.



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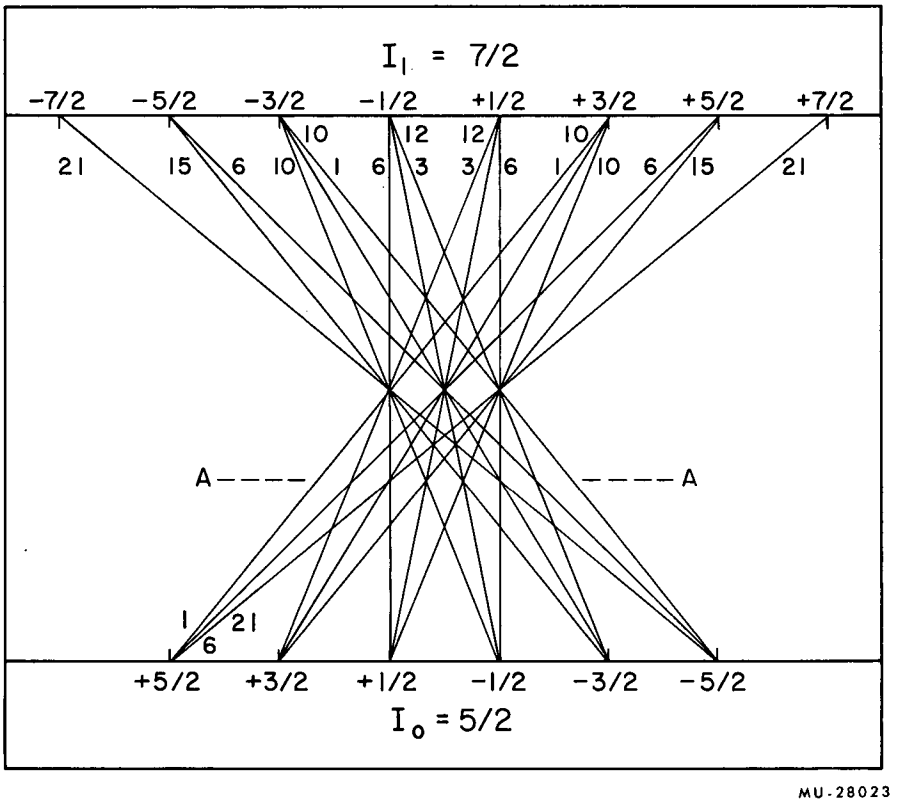

Fig. 4. The g-factor diagram for a dipole transition between two states of spins 5/2 and 7/2, having magnetic moments of the same sign. The line A-A fits the Eu^{151} spectrum. Numbers near lines denote relative intensities.