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### Calculation of Optical Transitions in $\text{NiI}_2$ and $\text{CoI}_2$ under Pressure

A.J.R. da Silva and L.M. Falicov

November 1991



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CALCULATION OF OPTICAL TRANSITIONS IN  
NiI<sub>2</sub> AND CoI<sub>2</sub> UNDER PRESSURE\*

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# Calculation of Optical Transitions in $NiI_2$ and $CoI_2$ under Pressure

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## ABSTRACT

A calculation of the electronic spectra of  $Co^{++}$  in insulating  $CoI_2$  and  $Ni^{++}$  in insulating  $NiI_2$  as a function of pressure is presented. The results depend crucially on the variation with pressure of the crystallographic ( $c/a$ ) and  $u$  parameters. Level crossings are expected as a function of increasing pressure, including a possible change in the symmetry of the ground state for  $NiI_2$ .

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# Calculation of Optical Transitions in $NiI_2$ and $CoI_2$ under Pressure

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## 1. INTRODUCTION

The layered compounds  $NiI_2$  and  $CoI_2$  have been, in the last two years, the subject of intensive study<sup>1-4</sup>. The main reason for that interest is that both substances were discovered to undergo an insulator-to-metal transition under high hydrostatic pressure. That transition is in both cases accompanied by a loss of magnetic ordering. In the case of  $CoI_2$  the transition is clearly hysteretic as a function of pressure<sup>4</sup>, and takes place between 9 and 13 GPa. For  $NiI_2$ , although the Néel temperature discontinuously drops from about 310 K to zero at 19 GPa, there is no detectable hysteresis or discontinuity in the crystal lattice parameters<sup>5</sup>, as measured by x-ray diffraction.<sup>1</sup>

The general behavior of both substances under pressure can be well described by the Falicov-Kimball model<sup>3,6</sup>. The differences between  $NiI_2$  and  $CoI_2$  are almost certainly related to the differences in electronic structure of the corresponding ions  $Ni^{++}$  and  $Co^{++}$ . This difference can be studied by investigating the optical properties<sup>7-10</sup>, especially their changes under pressure.

This paper presents a calculation of the crystal-field effects on the  $Ni^{++}$  and  $Co^{++}$  electronic energy levels in  $NiI_2$  and  $CoI_2$  under pressure. The calculation includes a "cubic" local field, its trigonal distortion, spin-orbit effects, and changes under pressure, the departure from "cubic environment" in particular.

Both  $NiI_2$  and  $CoI_2$  are layered compounds. They crystallize in the  $CdCl_2$  and  $CdI_2$  structures, respectively<sup>5</sup>. In both structures, close-packed hexagonal layers of  $M^{++}$  metal ions (indicated by lower-case letters), extending perpendicularly to the  $c$ -axis, are sandwiched between two layers of  $I^-$  ions (denoted by capital letters). In  $NiI_2$  the stacking is



whereas in  $CoI_2$  the stacking is



in all cases  $A, B, C$  and  $a, b, c$  indicate the three possible kinds of hexagonal layers.

The reported space group<sup>5,8</sup> for  $NiI_2$  is  $D_{3d}^5$ , and for  $CoI_2$  is  $D_{3d}^3$ . In both compounds the environment of each metal ion is octahedral, with a  $D_{3d}$  point symmetry, but close enough to  $O_h$  symmetry. The hexagonal lattice constants<sup>5</sup> are  $a=3.892 \text{ \AA}$  and  $c=19.634 \text{ \AA}$  for  $NiI_2$  (with three triple layers) and  $a=3.96 \text{ \AA}$  and  $c=6.65 \text{ \AA}$  for  $CoI_2$  (with only one triple layer).

The magnetic structure is similar in both compounds<sup>11</sup>. It is a helix of type 1, incommensurable for  $NiI_2$  and commensurable for  $CoI_2$ . Both structures can be approximated by ferromagnetic layers of metal ions which are coupled antiferromagnetically along the  $c$ -axis. At ordinary pressures the Néel temperatures are approximately 80 K and 10 K, respectively. For both compounds the Néel temperature increases with pressure, up to a critical pressure,  $p_c$ , beyond which the antiferromagnetism disappears<sup>1,4</sup> and the compounds become metallic.



The present work is concerned only with the electronic and optical properties of both metal ions, under pressure and below  $p_c$ , in the insulating phase. The calculations are for a single ion in the crystal-field approximation. The model and methods of solution are presented in Sec. 2. In Sec. 3 the results are discussed, and Sec. 4 contains the conclusions.

## 2. MODEL AND METHODS OF SOLUTION

The free-ion ground-state terms --  $^4F$  for  $Co^{++}$ , and  $^3F$  for  $Ni^{++}$  -- are the starting point in all crystal-field studies. These terms have a degeneracy of  $d = (2S + 1)(2L + 1)$ , i.e.,  $d = 28$  for  $Co^{++}$  and  $d = 21$  for  $Ni^{++}$ . This degeneracy is partially lifted by three distinct effects: (a) a "cubic" octahedral  $O_h$  field caused by a perfect regular-octahedron arrangement of the six  $I^-$ ; (b) a "trigonal"  $D_{3d}$  distortion originating from the more distant neighbors and the distortion of the nearest-neighbor environment from cubic (regular octahedral) symmetry; and (c) the spin-orbit interaction. Of these (a) is the largest effect; (b) and (c) are somewhat smaller than (a), and of similar order of magnitude<sup>10,12</sup>. The single-ion Hamiltonian can thus be written

$$H = H_{CF} + \lambda \mathbf{L} \cdot \mathbf{S} \quad (1)$$

Here  $\lambda$  is the spin-orbit coupling constant,  $\mathbf{L}$  the total orbital angular momentum,  $\mathbf{S}$  the total spin, and  $H_{CF}$  the crystal-field hamiltonian. With the choice of the three-fold symmetric  $c$ -axis as the polar  $z$ -axis,  $H_{CF}$  can be written as<sup>13,14</sup>

$$H_{CF} = - \sum_{i=1}^N \left\{ R Y_{20}(\theta_i, \phi_i) + Q_1 Y_{40}(\theta_i, \phi_i) + Q_2 \left[ Y_{43}(\theta_i, \phi_i) - Y_{4-3}(\theta_i, \phi_i) \right] \right\} \quad (2)$$

where  $N$  is the number of electrons in the  $3d$  free-ion shell -- 7 for  $Co^{++}$ , and 8 for  $Ni^{++}$  -- and  $Y_{lm}(\theta, \phi)$  are spherical harmonics. The parameters  $Q_1$  and  $Q_2$  are the strength of the cubic field;  $R$  is the strength of the trigonal distortion.

It should be noticed that the spin-orbit term in this model is isotropic. An anisotropic spin-orbit interaction is important to obtain an accurate fit of the theory to the experimentally observed values<sup>10,12</sup>; this anisotropic term is not necessary to examine the variation of the levels under pressure and it is not included here.

With  $\chi$  defined as the angle between the  $c$ -axis and the vector that joins the metal-ion and any particular first-neighbor  $I^-$  ion, the crystal-field parameters  $R$ ,  $Q_1$  and  $Q_2$  -- assumed to arise exclusively from the six first-neighbor anions -- can be written

$$R = 6 \sqrt{\pi/5} P_1 (3 \cos^2 \chi - 1) \quad , \quad (3a)$$

$$Q_1 = \frac{1}{2} \sqrt{\pi} P_2 (35 \cos^4 \chi - 30 \cos^2 \chi + 3) \quad , \quad (3b)$$

$$Q_2 = \sqrt{35\pi} P_2 (\cos \chi \sin^3 \chi) \quad . \quad (3c)$$

Standard application of crystal-field theory<sup>13-15</sup> for *point charges* yields for the parameters  $P_1$  and  $P_2$

$$P_1 = e^* |e| \int [f_{3d}(r)]^2 \frac{r_{<}^2}{r_{>}^3} r^2 dr \quad , \quad (4a)$$

$$P_2 = e^* |e| \int [f_{3d}(r)]^2 \frac{r_{<}^4}{r_{>}^5} r^2 dr \quad . \quad (4b)$$

Here  $e^*$  is the effective  $I^-$  charge,  $|e|$  is the magnitude of the electron charge,  $f_{3d}(r)$  is the radial function for the  $3d$  states in the metal ions and  $r_{<}$  ( $r_{>}$ ) is the smaller (larger) of the integration variable  $r$  and the cation-anion distance. Although the point-ion approximation and expressions (4) are *not directly used*<sup>14-17</sup> to calculate the parameters  $P_1$  and  $P_2$ , they can be fruitfully employed to obtain their correct signs. Since  $e^*$  is a negative charge and the integrals in (4) are positive-definite,  $P_1$  and  $P_2$  are expected to be negative; otherwise they are taken as adjustable so as to fit the experimental data.

In an  $O_h$  environment, a spinless  $F$  term splits into three levels<sup>18-20</sup>, two three-fold degenerate,  $T_{1g}$  and  $T_{2g}$ , and a nondegenerate one,  $A_{2g}$ . The irreducible representations of the  $O_h$  group are used to label them. With a  $D_{3d}$  trigonal distortion, both  $T_{1g}$  and  $T_{2g}$  split<sup>18,19</sup> into a doubly degenerate level and a nondegenerate one,

$$T_{1g} = e_g \oplus a_{2g} \quad ,$$

$$T_{2g} = e_g \oplus a_{1g} \quad ,$$

where the labels are those corresponding to the irreducible representations of the  $D_{3d}$  group.

Therefore, the  $F$  terms, under the influence of  $H_{CF}$ , split into five levels, with energies given by

$$E(a_{1g} : T_{2g}) = \eta \left[ \frac{1}{14} \sqrt{\frac{5}{\pi}} R + \frac{3}{14\sqrt{\pi}} Q_1 \right] \quad , \quad (8a)$$

$$E(e_g : T_{2g}) = \eta \left[ -\frac{3}{140} \sqrt{\frac{5}{\pi}} R - \frac{3}{14\sqrt{\pi}} Q_1 \right] + \frac{\eta}{2} \left\{ \left[ \frac{3}{70} \sqrt{\frac{5}{\pi}} R - \frac{4}{7\sqrt{\pi}} Q_1 \right]^2 + \frac{10}{35\pi} (Q_2)^2 \right\}^{1/2} \quad , \quad (8b)$$

$$E(a_{2g} : T_{1g}) = \eta \left[ \frac{1}{140} \sqrt{\frac{5}{\pi}} R + \frac{9}{28\sqrt{\pi}} Q_1 \right] - \frac{\eta}{2} \left\{ \left[ -\frac{9}{70} \sqrt{\frac{5}{\pi}} R + \frac{3}{14\sqrt{\pi}} Q_1 \right]^2 + \frac{18}{7\pi} (Q_2)^2 \right\}^{1/2} \quad , \quad (8c)$$

$$E(e_g : T_{1g}) = \eta \left[ -\frac{3}{140} \sqrt{\frac{5}{\pi}} R - \frac{3}{14\sqrt{\pi}} Q_1 \right] - \frac{\eta}{2} \left\{ \left[ \frac{3}{70} \sqrt{\frac{5}{\pi}} R - \frac{4}{7\sqrt{\pi}} Q_1 \right]^2 + \frac{10}{35\pi} (Q_2)^2 \right\}^{1/2} \quad , \quad (8d)$$

$$E(a_{2g} : A_{2g}) = \eta \left[ \frac{1}{140} \sqrt{\frac{5}{\pi}} R + \frac{9}{28\sqrt{\pi}} Q_1 \right]$$

$$+ \frac{\eta}{2} \left\{ \left[ -\frac{9}{70} \sqrt{\frac{5}{\pi}} R + \frac{3}{14\sqrt{\pi}} Q_1 \right]^2 + \frac{18}{7\pi} (Q_2)^2 \right\}^{1/2} \quad , (8e)$$

where  $\eta$  takes the value (+1) for  $CoI_2$  -- seven  $d$  electrons -- and (-1) for  $NiI_2$  -- eight  $d$  electrons. All these levels are still  $(2S+1)v$ - degenerate, with  $v=1$  for levels with  $a_g$  symmetry,  $v=2$  for levels with  $e_g$  symmetry,  $S=1$  for  $NiI_2$  and  $S=(3/2)$  for  $CoI_2$ .

The trigonal distortion disappears for  $\cos \chi_c = 1/\sqrt{3}$  or  $\chi_c = 54.7^\circ$ ; at that angle the six nearest-neighbor anions make a perfect, regular octahedron. In that case the trigonal component vanishes --  $R=0$ . For that value of the parameter  $\chi$ , the crystal-field levels are identified by the symmetry of the  $O_h$  group, *i.e.*, the second label in the five equations (8). The resulting energies are

$$E(a_{2g} : T_{1g}) = E(e_g : T_{1g}) = \eta P_2 \quad ,$$

$$E(a_{1g} : T_{2g}) = E(e_g : T_{2g}) = -\eta P_2/3 \quad ,$$

$$E(a_{2g} : A_{2g}) = -2\eta P_2 \quad .$$

Experimental data clearly indicate that the ground state of  $Co^{++}$  in  $CoI_2$ , derives from the  $T_{1g}$  cubic level<sup>11</sup> whereas for  $Ni^{++}$  in  $NiI_2$  it derives from the  $A_{2g}$  cubic level<sup>8</sup>. These data confirm that  $P_2$  must be negative, in agreement with the point-ion approximation (4).

The spin-orbit interaction has the effect, for  $Co^{++}$  in  $CoI_2$  with an odd number of electrons, of producing a manifold of 14 Kramers doublets, which are classified according the labels of the irreducible representations of the  $D_{3d}$  double group<sup>12</sup>. All the resulting levels are either a group doublet  $\gamma_{4g}$  or a time-reversal-degenerate doublet  $\gamma_{56g} = \gamma_{5g} \oplus \gamma_{6g}$ :

$${}^4a_{1g} = \gamma_{4g} \oplus \gamma_{56g} \quad ,$$

$${}^4a_{2g} = \gamma_{4g} \oplus \gamma_{56g} \quad ,$$

$${}^4e_g = 3\gamma_{4g} \oplus \gamma_{56g} \quad .$$

For  $Ni^{++}$  in  $NiI_2$ , which has an even number of electrons, the effect of the spin-orbit interaction is to produce also a manifold of 14 levels, but composed in this case of 7 non-degenerate levels (either  $a_{1g}$  or  $a_{2g}$ ) and 7 doubly degenerate levels ( $e_g$ ) that are labeled according to the ordinary irreducible representations of  $D_{3d}$ :

$${}^3a_{1g} = e_g \oplus a_{2g} \quad ,$$

$${}^3a_{2g} = e_g \oplus a_{1g} \quad ,$$

$${}^3e_g = 2e_g \oplus a_{1g} \oplus a_{2g} \quad .$$

The total hamiltonian, written using the eigenvectors obtained from the diagonalization of  $H_{CF}$ , has been diagonalized numerically. The levels thus obtained are functions of the four parameters  $\lambda$ ,  $P_1$ ,  $P_2$  and  $\chi$ . The values of these parameters are discussed in the next section.

### 3. RESULTS

The values of the parameters are determined at normal pressure by fitting the calculated energy values to the experimental ones. For  $CoI_2$ , the experimental values are from the Raman scattering data of Mischler *et al.*<sup>10</sup>. The angle  $\chi$  is taken from crystal parameter data<sup>5,21,22</sup> to be  $\chi(p=0) = 54.0^\circ$ . The other three parameters were obtained by a least-square fit. The results, together with the experimental values, are given in Table I.

Under pressure, the most sensitive parameter is  $\chi$ . This fact is supported by experiments<sup>23</sup> in  $NiI_2$ , discussed below. As pressure is applied  $\chi$  varies significantly, and may cross the value  $\chi_c = 54.7^\circ$ , where the trigonal crystal-field vanishes. Because of the additional symmetry at this point ( $O_h$  instead of  $D_{3d}$ ) one expects increased degeneracies and level-crossings.

Figure 1 shows the behavior of the first five excited levels as  $\chi$  (or the pressure) varies. The ground state, which is always of symmetry  $\gamma_{4g}$ , is taken as the zero of energy. All six levels are associated with the  ${}^4T_{1g}$  cubic level. As predicted by symmetry, some of the levels cross at  $\chi_c$ . Since those levels correspond to different trigonal symmetries, they can also cross at other points (accidental degeneracies). In fact they do, and they are almost degenerate between  $\chi_c$  and the angle of the second crossing (see Fig. 1). Therefore, as pressure is applied, the following features are expected: (a) merging of the  $\gamma_{4g}$  and  $\gamma_{56g}$  lines; (b) a pressure range where they are close in energy; and (c) possibly two values of pressure where the lines are truly degenerate.

In Fig. 2, the higher excited states associated with the  ${}^4T_{2g}$  cubic level are shown as a function of the angle  $\chi$ . Here again the expected crossings between the  $\gamma_{4g}$  and  $\gamma_{56g}$  levels<sup>24</sup> are observed at  $\chi_c$ . The general behavior of the levels is however more involved. At normal pressures, the trigonal component of the crystal field is larger than the spin-orbit coupling, and the levels split in a lower multiplet of two levels, associated with the  $(a_{1g} : T_{2g})$  level, and an upper multiplet of four levels related to the  $(e_g : T_{2g})$  level. As pressure is applied, the angle  $\chi$  varies in such a way as to decrease the trigonal distortion, and the two multiplets merge at  $\chi = \chi_c$ . At  $\chi_c$  some of the levels cross. As pressure is further increased the trigonal distortion reappears, and the two multiplets once again separate, but now with the  $(a_{1g} : T_{2g})$  levels higher in energy than the  $(e_g : T_{2g})$  levels. The highest energy excited states derived from the  ${}^4F$  free-ion term are shown in Fig.3. They correspond to the  ${}^4A_{2g}$  cubic level, and as a function of pressure they cross only when the trigonal component of the crystal field vanishes.

It is important to stress that all these crossings at  $\chi_c$  are independent of the particular values of the parameters and of their variation under pressure. These crossings are symmetry induced and occur if, upon application of pressure, the angle  $\chi$  passes through the value  $\chi_c$ . Level crossings at values of  $\chi$  other than  $\chi_c$  may or may not

exist, and their existence and location are sensitive functions of the parameters  $P_1$ ,  $P_2$  and  $\lambda$ .

It is also important to remark that the variations of the  $(c/a)$  ratio (determined from the Bragg scattering angles), and internal-structure parameter  $u$  (which requires careful measurement of the x-ray intensities as function of pressure) influence greatly the behavior of the spectrum. If  $u$  increases appreciably,  $\chi$  will not reach the value  $\chi_c$  at any pressure. In fact the critical angle  $\chi_c$  is reached whenever

$$(c/a) u = 6^{-1/2} = 0.408 \quad .$$

At  $p=0$  the product  $(c/a) u$  takes the value 0.420 in  $CoI_2$ . In  $NiI_2$  and  $FeI_2$  it is known that  $(c/a)$  decreases with increasing pressure<sup>23</sup>. It is reasonable to assume that the same situation applies to  $CoI_2$ . If the variation were identical to that of  $NiI_2$ , and  $u$  were to remain constant, the critical value  $\chi_c$  would be reached at approximately  $p=5 \text{ GPa}$ . On the other hand, if  $u$  were to increase from  $u=0.25$  to  $u=0.263$  at relatively low pressures, and the  $(c/a)$  ratio were to behave similarly to that of  $NiI_2$ , then the critical angle  $\chi_c$  would never be reached.

The variation of  $u$  with pressure is not easy to measure. In addition, since the equilibrium value of  $u$  at a given pressure is intimately related to charge transfers, theoretical estimates of its value are difficult to make. For the time being the variation of  $u$  with pressure remains unknown, and should be considered a "fitting" parameter.

For  $NiI_2$  the analysis of the spectrum is more complicated for two reasons: (1) the published near-infrared spectroscopic results<sup>8</sup> are less complete than those<sup>10</sup> for  $CoI_2$ ; and (2) two mutually inconsistent experimental values for the internal crystal parameter  $u$  at normal pressure,

$$u = 0.250 \quad , \quad u = 0.256 \quad ,$$

are reported<sup>5,22</sup> in the literature, which yield two values<sup>21</sup> of the angle  $\chi$  ( $p=0$ ).

Kuindersma *et al.*<sup>8</sup> report only three observed spectroscopic lines where one expects thirteen. These authors try to fit the experimental results by including only the cubic crystal-field and the spin-orbit interaction, *i.e.*, implicitly assuming that the trigonal component of the crystal field is smaller than the spin-orbit coupling, and negligible. Actually, the opposite seems to be true, and reasonable fits are obtained if the experimental lines are identified with the crystal-field levels in a cubic environment with trigonal distortion, without any spin-orbit interaction. This latter conclusion was reached by Pollini *et al.*<sup>25</sup>, in connection with  $NiBr_2$  and  $NiCl_2$ . Here the Hamiltonian parameters were obtained by a least-square-fit procedure. In the first approximation the spin-orbit interaction is neglected, and  $P_1$  and  $P_2$  are determined from the experimental data.<sup>8</sup> The calculations were performed for the two reported values of the internal parameters  $u$ , and the results are presented in Table II. It should be noted that the experimentally observed lines correspond to different symmetry assignments, depending on the chosen value of  $u$  ( $p=0$ ). The spin-orbit coupling parameter  $\lambda$  was chosen to be  $\lambda = -250 \text{ cm}^{-1}$ . This value was obtained by multiplying the  $\lambda$  for  $CoI_2$  by the ratio of the *atomic* spin-orbit parameters  $(\lambda_{Ni} / \lambda_{Co}) = 1.78$ . The effect of pressure on the spectrum is, once again, studied by varying the angle  $\chi$  while keeping the other parameters unchanged.

Two very different results emerge. If  $u = 0.256$ , as reported in reference 22,  $\chi$  is larger than  $\chi_c$  for all pressures, and no level crossings are expected as function of the applied pressure. On the other hand, if  $u = 0.250$ , as quoted in reference 5, the value of  $\chi(p=0)$  is smaller than  $\chi_c$  and, for sensible variations of  $u$  and  $(c/a)$  with pressure, some levels are expected to cross, as shown in Figs. 4 and 5. Note (Fig. 4) that the ground state changes as a function of the angle  $\chi$  at  $\chi_c$ . Therefore for  $u = 0.250$  a change in the ground-state symmetry is expected as a function of pressure; no such change should take place if  $u = 0.256$ . Figure 5 shows the levels associated with the intermediate cubic level  ${}^3T_{2g}$ , and the behavior of the lines is very similar to that



found in  $CoI_2$  (Fig. 2). The higher excited states, those derived from the  ${}^3T_{1g}$  cubic level, are not shown. They fall in a range of energies where interaction with other terms<sup>25</sup> in the atomic spectrum becomes relevant, and the single-term approximation,  ${}^3F$ , is no longer valid.

It is important to remark, once again, that whenever  $\chi$  passes through the value  $\chi_c$ , level crossings are to be expected, regardless of the values of the parameters. In the case of  $NiI_2$  this results in a change of symmetry of the ground state, with a consequent major restructuring of all absorption lines.

#### 4. CONCLUSIONS

The effect of pressure on the excitation energies for the levels derived from the  $F$  ground-state terms of  $Co^{++}$  and  $Ni^{++}$  in  $CoI_2$  and  $NiI_2$  has been studied in the crystal-field approximation. The field includes a strong cubic term, a small trigonal distortion, and the spin-orbit interaction. It was assumed that the main effect of pressure in the system results in a variation of the metal-iodine bond angle  $\chi$ . This variation is supported by experimental results in  $NiI_2$ , as shown in Table III.

It was found that in  $CoI_2$ , as pressure is applied, some of the levels will cross at  $\chi_c = 54.7^\circ$ . At this point the trigonal distortion completely vanishes, increasing the crystal-field hamiltonian symmetry. This result is independent of the hamiltonian parameters and their behavior under pressure.

For  $NiI_2$ , the results depend on the value of the parameter  $u$  at normal pressure. If  $u(p=0) = 0.256$ , one of the reported values<sup>22</sup>, the angle  $\chi$  is greater than  $\chi_c$  at ordinary pressure, and it is unlikely that it could decrease in value at higher pressures. On the other hand, if  $u(p=0) = 0.250$ , the other value in the literature<sup>5</sup>, a behavior similar to that found in  $CoI_2$  is to be expected. Spectroscopic measurements on  $NiI_2$  under pressure might help to elucidate details of its crystal structure.

Similar considerations could be applied to  $FeI_2$ . From the reported crystal structure<sup>5,21</sup> the angle  $\chi$  at normal pressure is equal to  $54.1^\circ$ , a value smaller than  $\chi_c$ . If, once again,  $FeI_2$  behaves similarly to  $NiI_2$  under pressure,  $\chi$  should cross the value  $\chi_c$  at reasonably accessible pressures. Under these conditions any quadrupole distortion in the Mössbauer spectrum should vanish. Such measurements are now underway<sup>23</sup>.

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- 20 In this contribution the following notation is used for the inversion-symmetric (subindex  $g$ ) representations of the various groups. For the single-valued (spinless) representations of  $O_h$ : one-dimensional representations  $A_{1g}$  and  $A_{2g}$ ; two-dimensional representation  $E_g$ ; three-dimensional representations  $T_{1g}$  and  $T_{2g}$ . For the single-valued (spinless) representations of  $D_{3d}$ : one-dimensional representations  $a_{1g}$  and  $a_{2g}$ ; two-dimensional representation  $e_g$ . For the double-valued (spin  $\frac{1}{2}$ ) representations of  $D_{3d}$ : two-dimensional representation  $\gamma_{4g}$ , and the Kramers doublet  $\gamma_{56g} = \gamma_{5g} \oplus \gamma_{6g}$ .
- 21 In the hexagonal notation, and given the lattice constants  $a$  and  $c$ , and the internal parameter  $u$ , the angle  $\chi$  is given by the expression

$$\chi = \tan^{-1} \frac{\sqrt{3} a}{3u c}$$

for  $CoI_2$ , and by

$$\chi = \tan^{-1} \frac{\sqrt{3} a}{(1-3u) c}$$

for  $NiI_2$ . At normal pressure,  $u$  is reported in Ref. 5 to be equal to 0.25 for  $CoI_2$ . For  $NiI_2$  the value  $u = 0.250$  is reported in Ref. 5, and the value  $u = 0.256$  in Ref. 22. Both values are used in this contribution.

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- <sup>24</sup> It should be noted that the second and third levels in Figure 2 cross each other twice at angles very near each other, so that for most of the range of  $\chi$  the symmetry ordering of the first three levels derived from  ${}^4T_{2g}$  remains unchanged:  $E(\gamma_{4g}) < E(\gamma_{5,6g}) < E(\gamma_{4g})$ .
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Table I. Experimental<sup>10</sup> and fitted energies for the  $Co^{++}$  electronic multiplets derived from the  ${}^4T_{1g}$  cubic ground-state level in  $CoI_2$  at normal pressure. All energies and parameters are in  $cm^{-1}$ .

Electronic State		Experiment	Fitted value $u = 0.25$
Trigonal Field	Spin-Orbit		
${}^4a_{2g}$	$\gamma_{4g}$	0	0 (0 %)
${}^4a_{2g}$	$\gamma_{56g}$	220	227 (+3.0 %)
${}^4e_g$	$\gamma_{4g}$	327	354 (+8.3 %)
${}^4e_g$	$\gamma_{4g}$	882	766 (-13.1 %)
${}^4e_g$	$\gamma_{56g}$	895	802 (-10.4 %)
${}^4e_g$	$\gamma_{4g}$	956	928 (-2.9 %)
Parameters			
	$P_1$		- 67,000
	$P_2$		- 4,200
	$\lambda$		- 140
	$\chi(p=0)$		54.0°

Table II. Experimental<sup>8</sup> and fitted energies for the  $Ni^{++}$  electronic levels in  $NiI_2$  at normal pressure. The symmetry of the ground state depends on the value of  $u$ , as discussed in the text. Spin-orbit interaction is neglected in the determination of  $P_1$  and  $P_2$ . All energies and parameters are in  $cm^{-1}$ .

Table II

Electronic State		Experiment	Fitted value $u = 0.250$
Cubic Field	Trigonal Field		
${}^3A_{2g}$	${}^3a_{2g}$	0	0 (0 %)
${}^3T_{2g}$	${}^3e_g$	7,350	7,274 (- 1.0 %)
${}^3T_{2g}$	${}^3a_{1g}$	8,050	7,974 (- 0.9 %)
Parameters			
	$P_1$		- 31,000
	$P_2$		- 4,500
	$\lambda$		- 250
	$\chi(p=0)$		54.0°
Electronic State		Experiment	Fitted value $u = 0.256$
Cubic Field	Trigonal Field		
${}^3A_{2g}$	${}^3a_{2g}$	0	0 (0 %)
${}^3T_{2g}$	${}^3a_{1g}$	7,350	7,358 (+ 0.1 %)
${}^3T_{2g}$	${}^3e_g$	8,050	8,071 (+ 0.3 %)
Parameters			
	$P_1$		- 23,000
	$P_2$		- 4,700
	$\lambda$		- 250
	$\chi(p=0)$		55.9°



Table III. Hexagonal lattice parameters  $a$  and  $c$ , as reported in Ref. 23, for  $NiI_2$  at three values of pressure. The angle  $\chi$  is obtained<sup>21</sup> from these lattice parameters, under the assumption of constant internal parameter  $u = 0.250$  (Ref. 5) or  $u = 0.256$  (Ref. 22).

Pressure (GPa)	0	7	19
$a$ (Å)	3.93	3.77	3.63
$c$ (Å)	19.8	18.2	16.9
$\chi$ for $u = 0.250$	54.0°	55.1°	56.1°
$\chi$ for $u = 0.256$	55.9°	57.0°	57.9°

## FIGURE CAPTIONS

### Figure 1.

Energy levels of  $Co^{++}$  in  $CoI_2$ , derived from the  ${}^4T_{1g}$  cubic level, plotted as a function of the angle  $\chi$ . The ground state is always of symmetry  $\gamma_{4g}$  and is taken as the zero of energy. The value  $\chi_c = 54.7^\circ$  corresponds to vanishing trigonal distortion. At normal pressure  $\chi(p=0) = 54.0^\circ$ . Level crossovers are shown with open circles. All the parameters are kept constant at the values listed in Table I. It should be noted that the second and third levels cross twice: first at  $\chi_c$ , and then at an angle very near and slightly larger than  $\chi_c$ .

### Figure 2.

Excitation energies from the  $\gamma_{4g}$  ground-state (taken as the energy zero) to the levels of  $Co^{++}$  in  $CoI_2$  derived from  ${}^4T_{2g}$  cubic level, as a function of the angle  $\chi$ . The value  $\chi_c = 54.7^\circ$  corresponds to vanishing trigonal distortion. At normal pressure  $\chi(p=0) = 54.0^\circ$ . Level crossovers are shown with open circles. All the parameters are kept constant at the values listed in Table I.

### Figure 3.

Excitation energies from the  $\gamma_{4g}$  ground-state (taken as the energy zero) to the levels of  $Co^{++}$  in  $CoI_2$  derived from  ${}^4A_{2g}$  cubic level, as a function of the angle  $\chi$ . The value  $\chi_c = 54.7^\circ$  corresponds to vanishing trigonal distortion. At normal pressure  $\chi(p=0) = 54.0^\circ$ . Level crossovers are shown with open circles. All the parameters are kept constant at the values listed in Table I.

**Figure 4.**

Lowest energy excitation from the ground state for the  $Ni^{++}$  ion in  $NiI_2$  as a function of the angle  $\chi$ . The ground state is of symmetry  $a_{1g}$  for  $\chi \leq \chi_c = 54.7^\circ$ , and of symmetry  $e_g$  for  $\chi \geq \chi_c$ . Both levels arise from the  ${}^3A_{2g}$  cubic level. At normal pressure  $\chi(p=0) = 54.0^\circ$ . Level crossovers are shown with open circles. All the parameters are kept constant at the values listed in Table II for  $u = 0.250$ .

**Figure 5.**

Excitation energies from the ground state for energy levels arising from the  ${}^3T_{2g}$  cubic level of the  $Ni^{++}$  ion in  $NiI_2$  as a function of the angle  $\chi$ . The ground state is of symmetry  $a_{1g}$  for  $\chi \leq \chi_c = 54.7^\circ$ , and of symmetry  $e_g$  for  $\chi \geq \chi_c$ . At normal pressure  $\chi(p=0) = 54.0^\circ$ . Level crossovers are shown with open circles. All the parameters are kept constant at the values listed in Table II for  $u = 0.250$ .

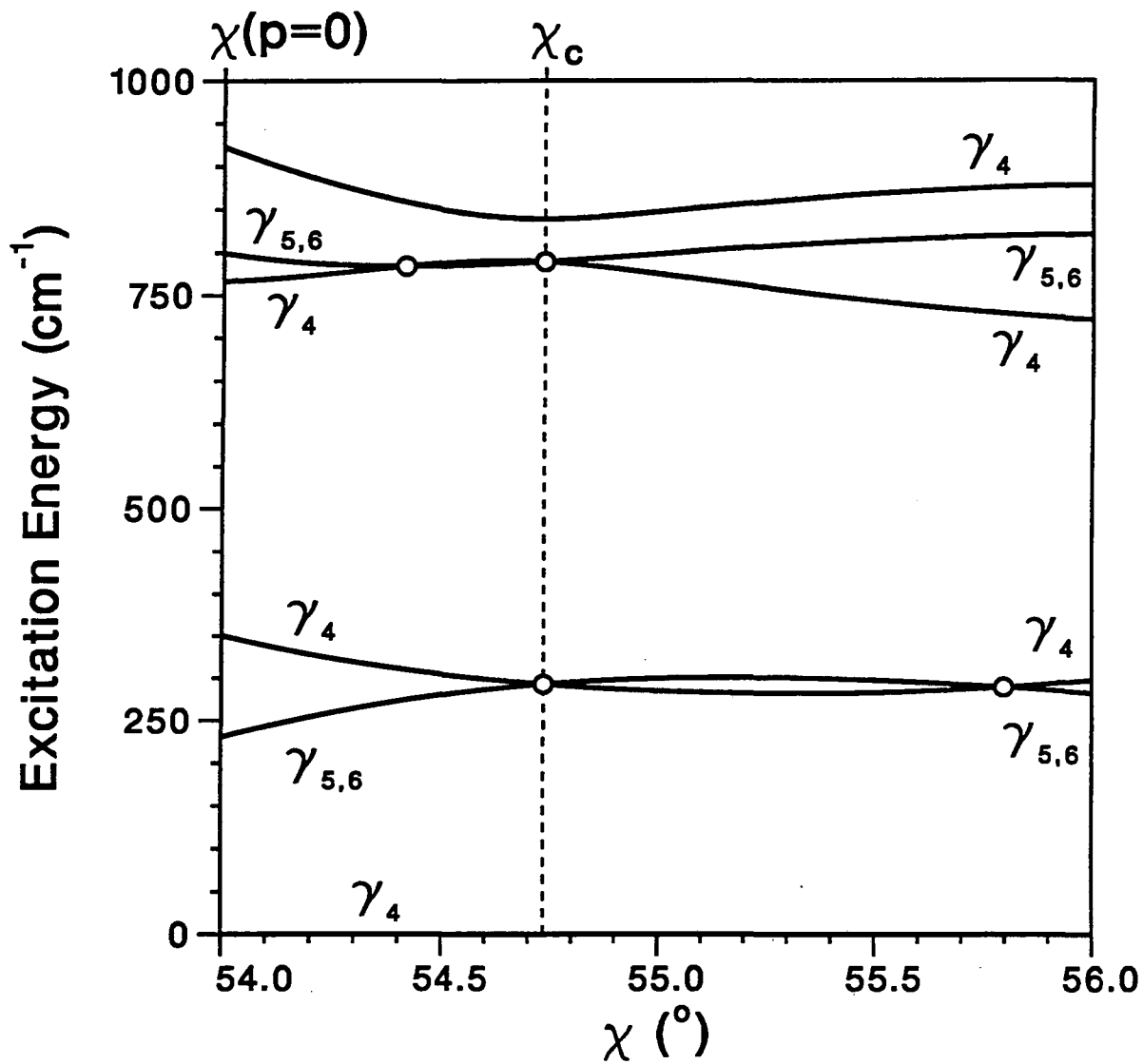


FIGURE 1

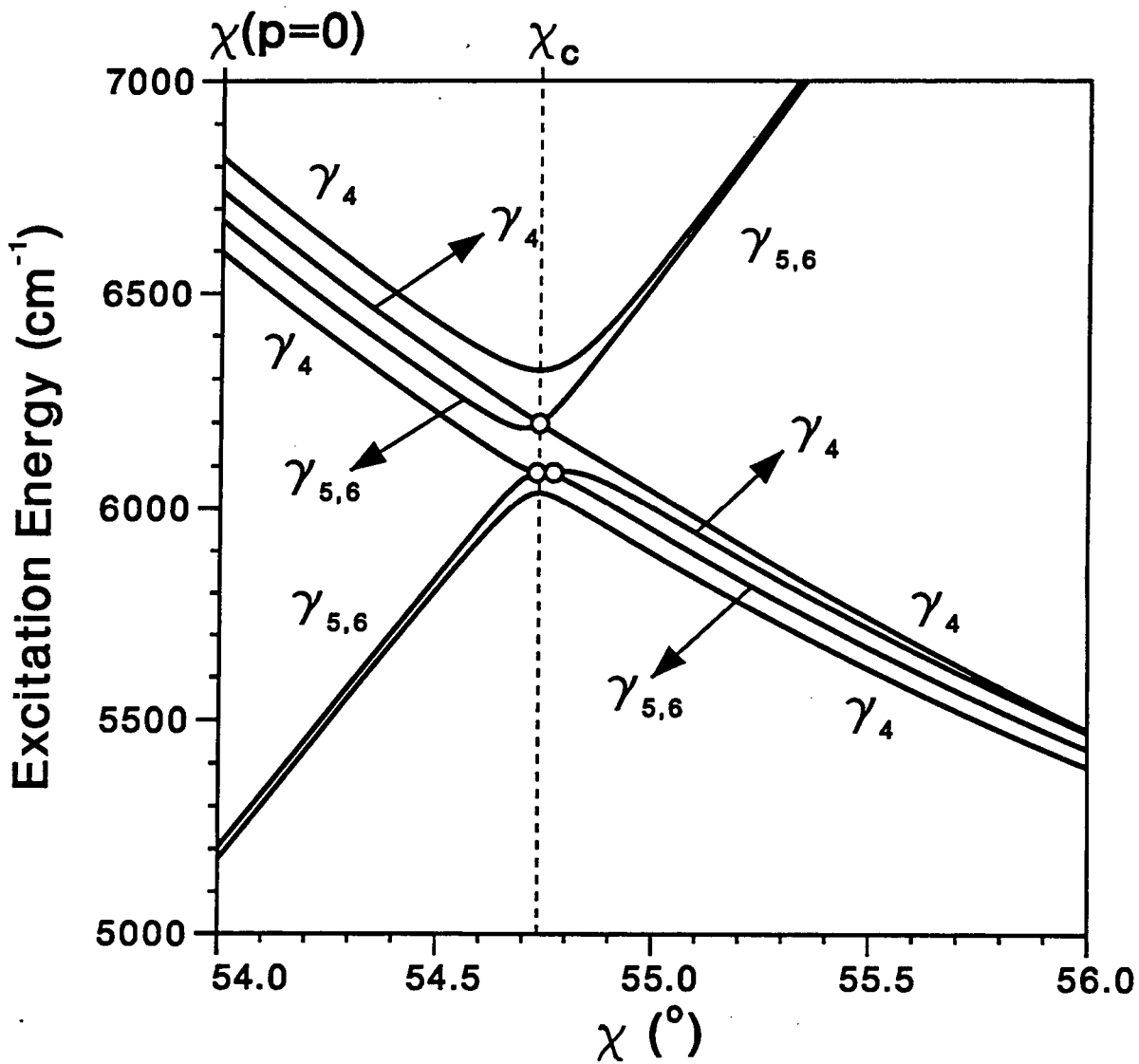


FIGURE 2

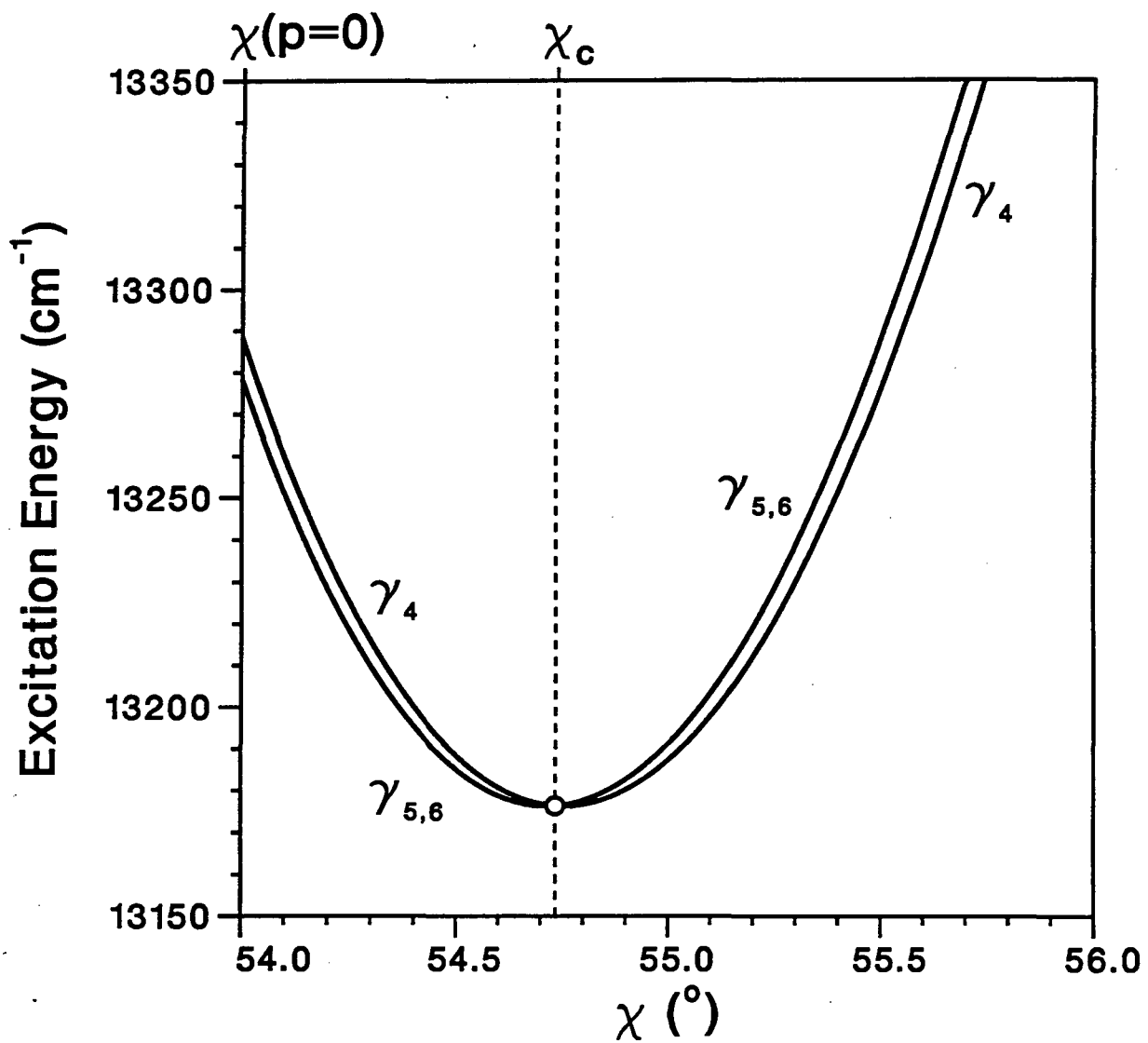


FIGURE 3

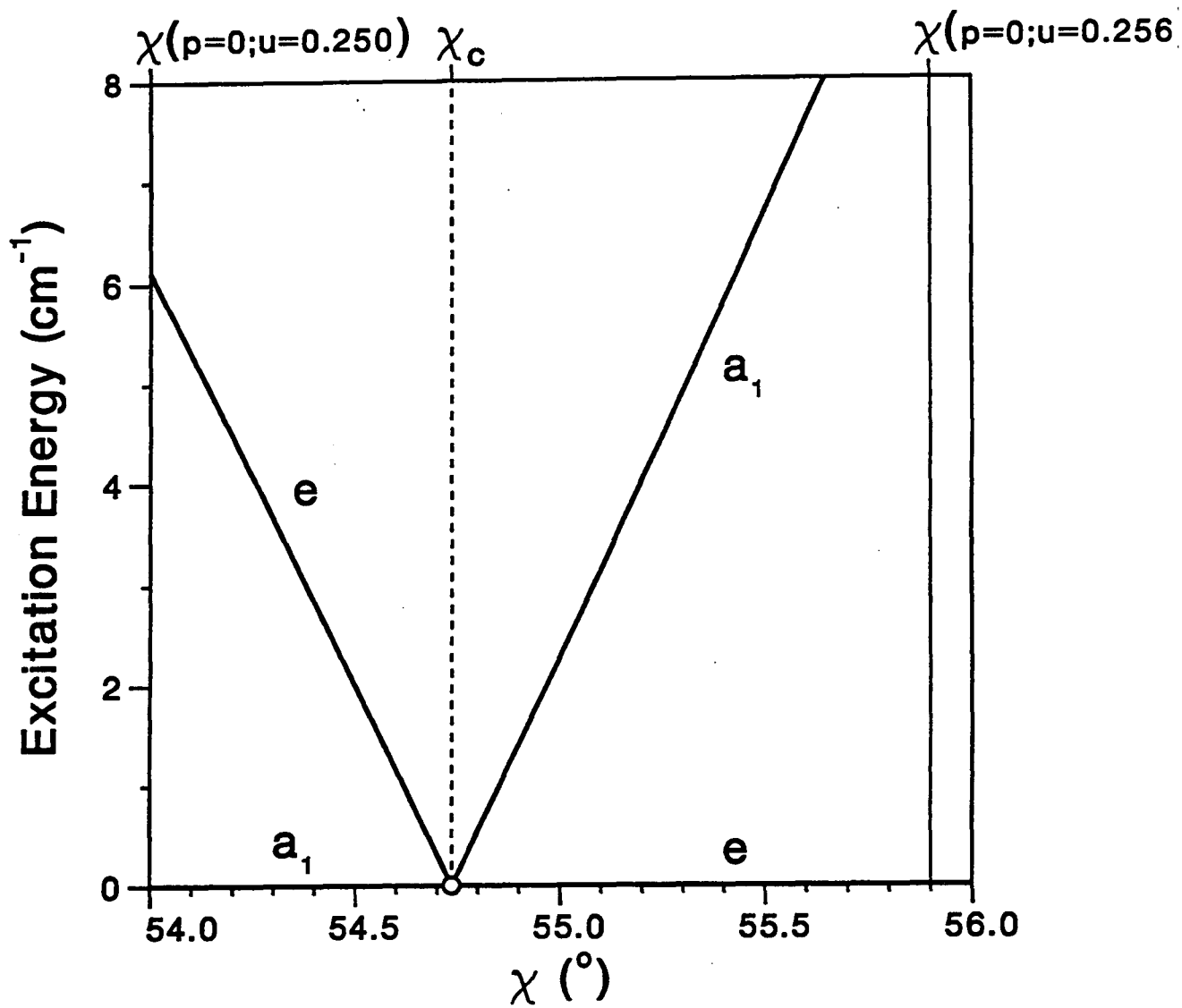


FIGURE 4

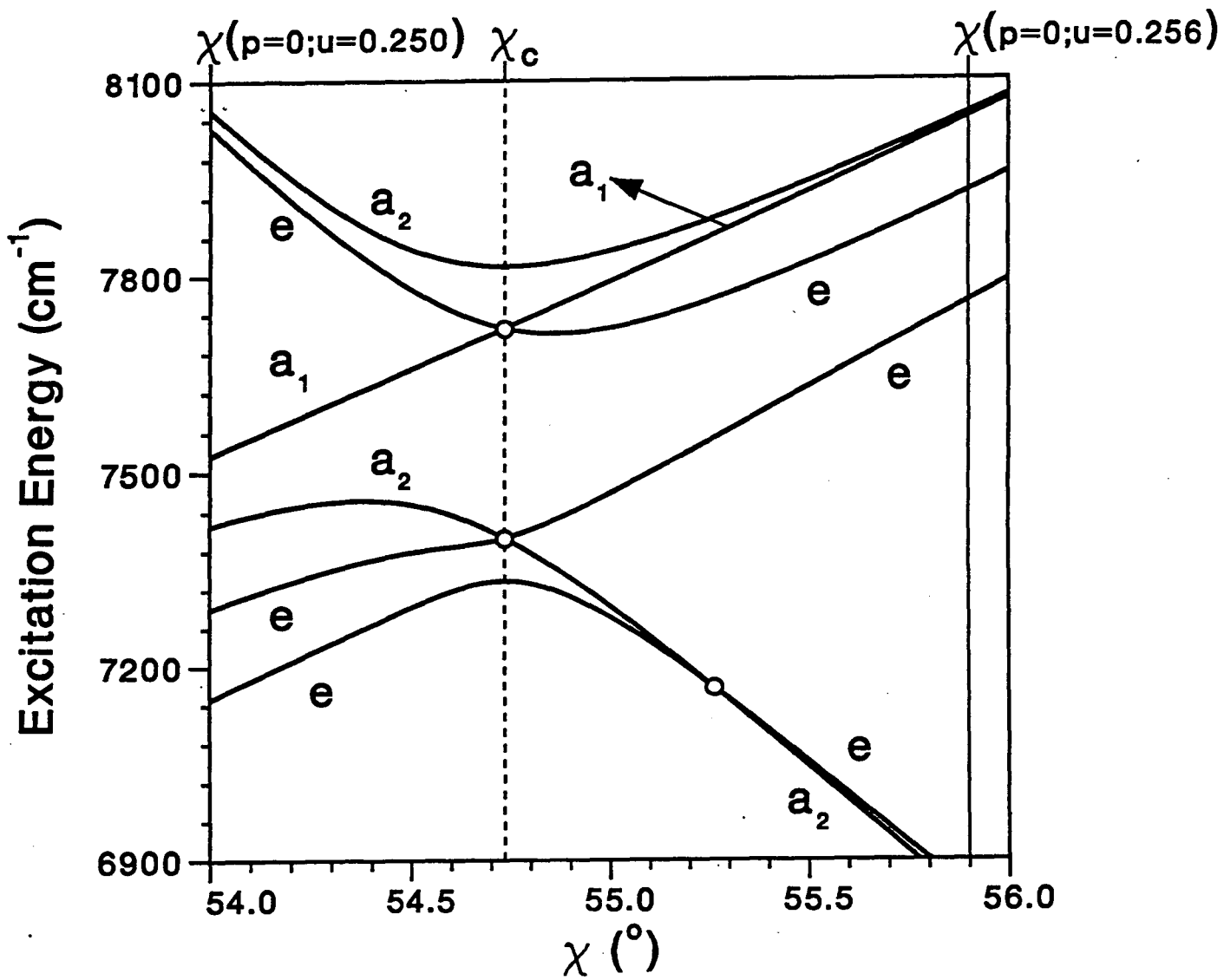


FIGURE 5



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