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Calculation of optical transitions in NiI_2 and CoI_2 under pressure

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A calculation of the electronic spectra of Co^{2+} in insulating CoI_2 and Ni^{2+} 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.

I. INTRODUCTION

The layered compounds NiI_2 and CoI_2 have been, in the past two years, the subject of intensive study.[1-4] 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,[4] 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,[5] as measured by x-ray diffraction.[1]

The general behavior of both substances under pressure can be well described by the Falicov-Kimball model.[3,6] The differences between NiI_2 and CoI_2 are almost certainly related to the differences in electronic structure of the corresponding ions Ni^{2+} and Co^{2+}. This difference can be studied by investigating the optical properties,[7-10] especially their changes under pressure.

This paper presents a calculation of the crystal-field effects on the Ni^{2+} and Co^{2+} 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 structure, respectively.[5] In both structures, close-packed hexagonal layers of M^{2+} 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

$$\cdots AcB\ CbA\ BaC\ AcB \cdots ,$$

whereas in CoI_2 the stacking is

$$\cdots AcB\ AcB\ AcB\ AcB \cdots ;$$

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

The reported space group[5,8] 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[5] are $a = 3.892$ Å and $c = 19.634$ Å for NiI_2 (with three triple layers) and $a = 3.96$ Å and $c = 6.65$ Å for CoI_2 (with only one triple layer).

The magnetic structure is similar in both compounds.[11] 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 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[1,4] 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. II. In Sec. III the results are discussed, and Sec. IV contains the conclusions.

II. MODEL AND METHODS OF SOLUTION

The free-ion ground-state terms—^4F for Co^{2+} and ^3F for Ni^{2+}—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^{2+} and $d = 21$ for Ni^{2+}. 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 a similar order of magnitude.[10,12] The single-ion Hamiltonian can thus be written

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

Here, λ is the spin-orbit coupling constant, $\mathbf{L}$ is the total orbital angular momentum, $\mathbf{S}$ is the total spin, and H_{CF} is the crystal-field Hamiltonian. With the choice of the threefold-symmetric c axis as the polar z axis, H_{CF} can be written as[13,14]

$$\begin{aligned} H_{\mathrm{CF}} = - \sum_{i=1}^{N} \{ & R Y_{20}(\theta_i,\phi_i) + Q_1 Y_{40}(\theta_i,\phi_i) \\ & + Q_2 [Y_{43}(\theta_i,\phi_i) - Y_{4-3}(\theta_i,\phi_i)] \} , \end{aligned} \tag{2}$$

where N is the number of electrons in the $3d$ free-ion shell—seven for Co^{2+} and eight for Ni^{2+}—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;[10,12] this anisotropic term is not necessary to examine the variation of the levels under pressure and it is not included here.

With χ 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

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

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

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

Standard application of crystal-field theory[13–15] for *point charges* yields for the parameters P_1 and P_2

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

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

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*[14–17] 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,[18–20] two threefold 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[18,19] into a doubly degenerate level and a nondegenerate one,

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

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

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

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

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

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

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

$$\begin{aligned} E(a_{2g}:A_{2g}) = {} & \eta \left[\frac{1}{140} \left[\frac{5}{\pi} \right]^{1/2} R + \frac{9}{28\sqrt{\pi}} Q_1 \right] \\ & + \frac{\eta}{2} \left\{ \left[-\frac{9}{70} \left[\frac{5}{\pi} \right]^{1/2} R + \frac{3}{14\sqrt{\pi}} Q_1 \right]^2 \right. \\ & \left. + \frac{18}{7\pi} (Q_2)^2 \right\}^{1/2} , \end{aligned} \tag{5e}$$

where η takes the value $(+1)$ for $\mathrm{CoI_2}$ (seven d electrons) and (-1) for $\mathrm{NiI_2}$ (eight d electrons). All these levels are still $(2S+1)\nu$-fold degenerate, with $\nu=1$ for levels with a_g symmetry, $\nu=2$ for levels with e_g symmetry, $S=1$ for $\mathrm{NiI_2}$, and $S=\frac{3}{2}$ for $\mathrm{CoI_2}$.

The trigonal distortion disappears for $\cos\chi_c = 1/\sqrt{3}$ or $\chi_c = 54.7°$; 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 χ, the crystal-field levels are identified by the symmetry of the O_h group, i.e., the second label in the Eqs. (5). The resulting energies are

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

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

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

Raman spectroscopy data[10] clearly indicate that the ground state of Co^{2+} in CoI_2 derives from the T_{1g} cubic level, whereas near-infrared spectra[8] for Ni^{2+} in NiI_2 point to a ground state derived from the A_{2g} cubic level. These data confirm that P_2 is negative, in agreement with the point-ion approximation (4).

The spin-orbit interaction has the effect, for Co^{2+} in CoI_2 with an odd number of electrons, of producing a manifold of 14 Kramers doublets, which are classified according to the labels of the irreducible representations of the D_{3d} double group.[12] All the resulting levels are either a group doublet γ_{4g} or a time-reversal-degenerate doublet $\gamma_{56g} = \gamma_{5g} \oplus \gamma_{6g}$:

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

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

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

For Ni^{2+} 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 nondegenerate levels (either a_{1g} or a_{2g}) and 7 doubly degenerate levels (e_g) that are labeled according to the ordinary irreducible representations of the D_{3d}:

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

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

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

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 λ, P_1, P_2, and χ. The values of these parameters are discussed in the next section.

III. 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, Lockwood, and Zwick.[10] The angle χ is taken from crystal parameter data[5,21,22] to be $\chi(p=0) = 54.0°$. The other three parameters were obtained by a least-squares fit. The results, together with the experimental values, are given in Table I.

Under pressure, the most sensitive parameter is χ. This fact is supported by experiments[23] in NiI_2, discussed below. As pressure is applied, χ varies significantly, and may cross the value $\chi_c = 54.7°$, 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 χ (or the pressure) varies. The ground state, which is always of symmetry γ_{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 χ_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 χ_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 γ_{4g} and γ_{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(a), the higher excited states associated with the $^4T_{2g}$ cubic level are shown as a function of the angle χ. Here again the expected crossings between the γ_{4g} and γ_{56g} levels[24] are observed at χ_c. The general behavior of the levels, however, is 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 χ varies in such a way as to decrease the trigonal distortion, and the two multiplets merge at $\chi = \chi_c$. At χ_c

TABLE I. Experimental (Ref. 10) and fitted energies for the Co^{2+} electronic multiplets derived from the $^4T_{1g}$ cubic ground-state level in CoI_2 at normal pressure. All energies and parameters are in units of cm^{-1}.

Electronic state			Fitted value
Trigonal field	Spin-orbit	Experiment	$u=0.25$
$^4a_{2g}$	γ_{4g}	0	0 (0%)
$^4a_{2g}$	γ_{56g}	220	227 (+3.0%)
^4e_g	γ_{4g}	327	354 (+8.3%)
^4e_g	γ_{4g}	882	766 (−13.1%)
^4e_g	γ_{56g}	895	802 (−10.4%)
^4e_g	γ_{4g}	956	928 (−2.9%)

Parameters	
P_1	−67 000
P_2	−4200
λ	−140
$\chi(p=0)$	54.0°

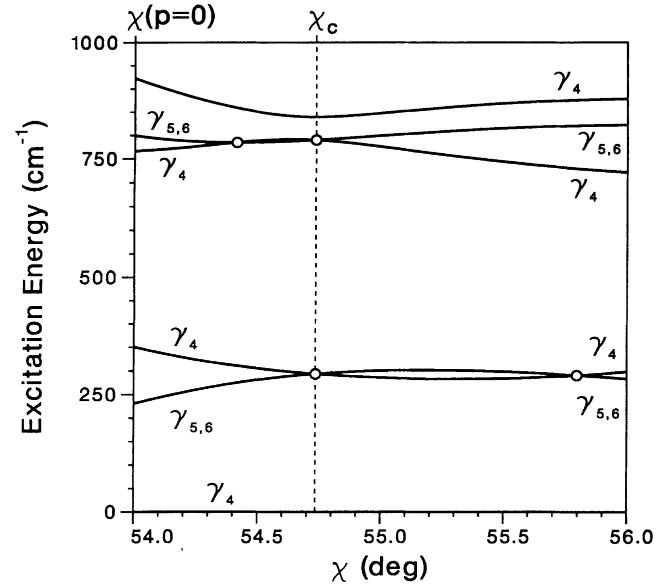

FIG. 1. Energy levels of Co^{2+} in CoI_2, derived from the $^4T_{1g}$ cubic level, plotted as a function of the angle χ. The ground state is always of symmetry γ_{4g} and is taken as the zero of energy. At normal pressure $\chi(p=0)=54.0°$. Level crossovers are shown with open circles. All the parameters are kept constant at the values listed in Table I.

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. 2(b). 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 χ_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 χ passes through the value χ_c. Level crossings at values of χ other than χ_c may or may not exist, and their existence and location are sensitive functions of the parameters P_1, P_2, and λ.

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 a function of pressure) influence greatly the behavior of the spectrum. If u increases appreciably, χ will not reach the value χ_c at any pressure. In fact, the critical angle χ_c is reached whenever

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

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.[23] 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 χ_c would be reached at approximately $p=5$ GPa. On the other hand, if u were to increase from $u=0.25$ to 0.263 at relatively low pressures, and the c/a ratio were to behave similarly to that of NiI_2, then the critical angle χ_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 compli-

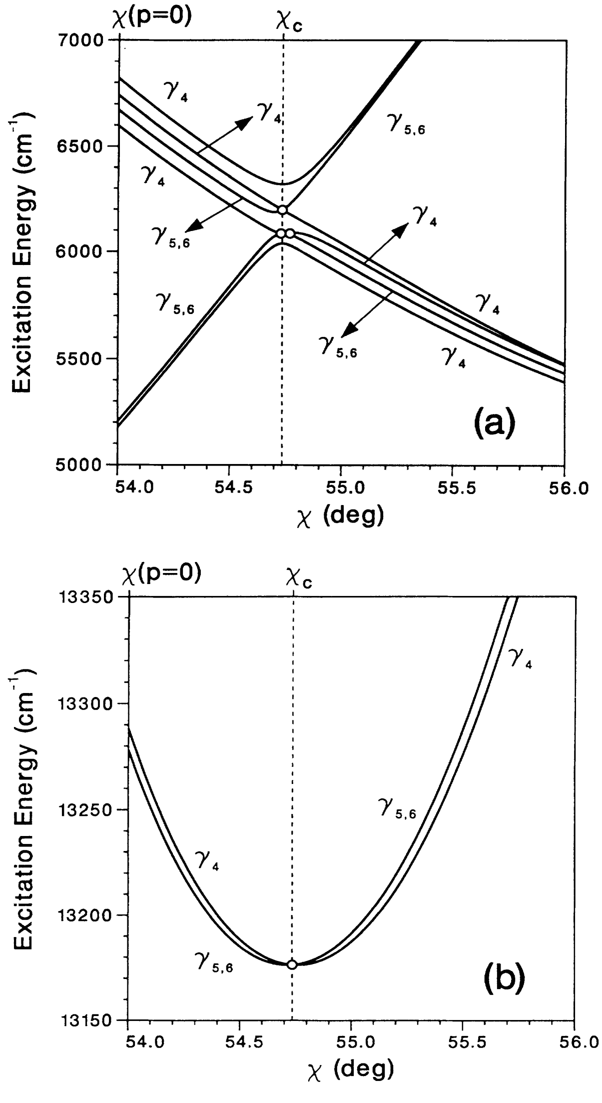

FIG. 2. Excitation energies from the γ_{4g} ground state (taken as the energy zero) to the levels of Co^{2+} in CoI_2, as a function of the angle χ. At normal pressure $\chi(p=0)=54.0°$. Level crossovers are shown with open circles. All the parameters are kept constant at the values listed in Table I. (a) The levels derived from the $^4T_{2g}$ symmetry; (b) the levels from $^4A_{2g}$. It should be noted that the second and third levels in (a) cross twice: first at χ_c, and then at an angle very near and slightly larger than χ_c.

cated for two reasons: (i) the published near-infrared spectroscopic results[8] are less complete than those[10] for CoI_2; and (ii) two mutually inconsistent experimental values for the internal crystal parameter u at normal pressure,

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

are reported[5,22] in the literature, which yield two values[21] of the angle $\chi(p=0)$, probably at different temperatures.[11]

Kuindersma, Boudewijn, and Haas[8] 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, Spinolo, and Benedek[25] in connection with $NiBr_2$ and $NiCl_2$. Here the Hamiltonian parameters were obtained by a least-squares-fitting procedure. In the first approximation the spin-orbit interaction is neglected, and P_1 and P_2 are determined from the experimental data.[8] 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 λ was chosen to be $\lambda = -250\ \text{cm}^{-1}$. This value was obtained by multiplying the λ 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 χ while keeping the other parameters unchanged.

Two very different results emerge. If $u = 0.256$, as reported in Ref. 22, χ is larger than χ_c for all pressures, and no level crossings are expected as a function of the applied pressure. On the other hand, if $u = 0.250$, as quoted in Ref. 5, the value of $\chi(p=0)$ is smaller than χ_c and, for sensible variations of u and c/a with pressure, some levels are expected to cross, as shown in Figs. 3 and 4. Note (Fig. 3) that the ground state changes as a function of the angle χ at χ_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 4 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(a)]. 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[25] 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 χ passes through the value χ_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.

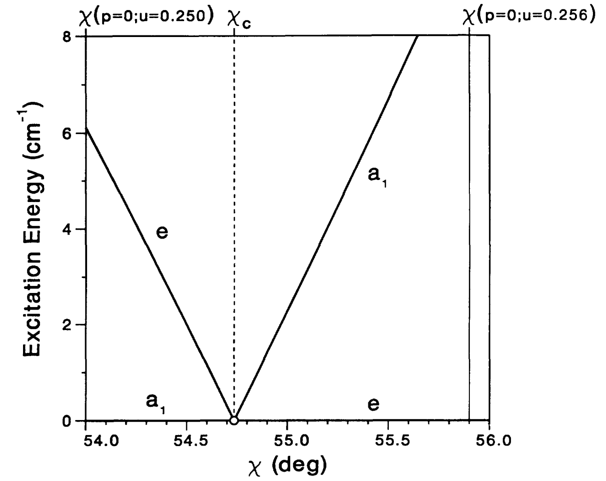

FIG. 3. Lowest-energy excitation from the ground state for the Ni^{2+} ion in NiI_2 as a function of the angle χ. The ground state is of symmetry a_{1g} for $\chi \le \chi_c = 54.7°$, and of symmetry e_g for $\chi \ge \chi_c$. Both levels arise from the $^3A_{2g}$ cubic level. At normal pressure $\chi(p=0)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

TABLE II. Experimental (Ref. 8) and fitted energies for the Ni^{2+} 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. All energies and parameters are in units of cm^{-1}.

Electronic state		$u = 0.250$		$u = 0.256$	
Cubic field	Trigonal field	Experiment	Fitted value	Experiment	Fitted value
$^3A_{2g}$	$^3a_{2g}$	0	0 (0%)	0	0 (0%)
$^3T_{2g}$	^3e_g	7350	7274 (−1.0%)	8050	8071 (+0.3%)
$^3T_{2g}$	$^3a_{1g}$	8050	7974 (−0.9%)	7350	7358 (+0.1%)
Parameters					
P_1		−31 000		−23 000	
P_2		−4500		−4700	
λ		−250		−250	
$\chi(p=0)$		54.0°		55.9°	

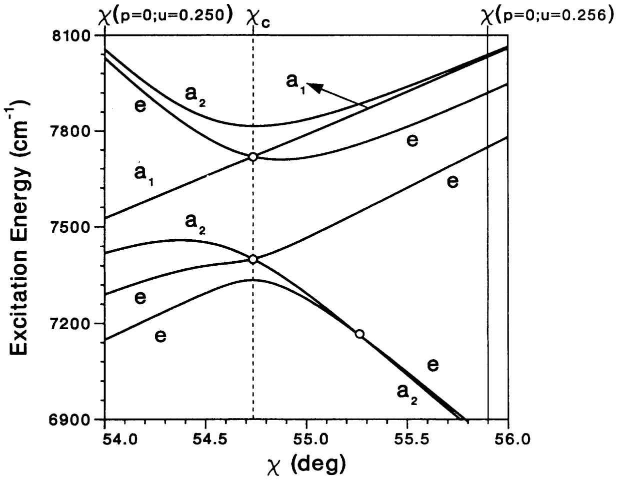

FIG. 4. Excitation energies from the ground state for energy levels arising from the $^3T_{2g}$ cubic level of the Ni^{2+} ion in NiI_2 as a function of the angle χ. The ground state is of symmetry a_{1g} for $\chi \leq \chi_c = 54.7°$, and of symmetry e_g for $\chi \geq \chi_c$. At normal pressure $\chi(p=0)=54.0°$. Level crossovers are shown with open circles. All the parameters are kept constant at the values listed in Table II for $u=0.250$.

IV. CONCLUSIONS

The effect of pressure on the excitation energies for the levels derived from the F ground-state terms of Co^{2+} and Ni^{2+} 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 χ. 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 $\chi_c = 54.7°$. 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.

TABLE III. Hexagonal lattice parameters a and c, as reported in Ref. 23, for NiI_2 at three values of pressure. The angle χ is obtained (Ref. 21) 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
χ for $u=0.250$	54.0°	55.1°	56.1°
χ for $u=0.256$	55.9°	57.0°	57.9°

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,[22] the angle χ is greater than χ_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,[5] 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[5,21] the angle χ at normal pressure is equal to 54.1°, a value smaller than χ_c. If, once again, FeI_2 behaves similarly to NiI_2 under pressure, χ should cross the value χ_c at reasonably accessible pressures. Under these conditions any quadrupole distortion in the Mössbauer spectrum should vanish. Such measurements are now underway.[23]

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[1] M. P. Pasternak, R. D. Taylor, A. Chen, C. Meade, L. M. Falicov, A. Giesekus, R. Jeanloz, and P. Y. Yu, Phys. Rev. Lett. **65**, 790 (1990).

[2] A. Giesekus and L. M. Falicov, Phys. Rev. B **44**, 10 449 (1991).

[3] J. K. Freericks and L. M. Falicov, Phys. Rev. B **45**, 1896 (1992).

[4] M. P. Pasternak, R. D. Taylor, and R. Jeanloz (private communication).

[5] R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1963), Vol. I.

[6] L. M. Falicov and J. C. Kimball, Phys. Rev. Lett. **22**, 997, (1969); R. Ramirez, L. M. Falicov, and J. C. Kimball, Phys. Rev. B **2**, 3383, (1970); L. M. Falicov, C. E. T. Gonçalves da Silva, and B. Huberman, Solid State Commun. **10**, 455 (1972).

[7] S. Antoci and L. Mihich, Phys. Rev. B **18**, 5768 (1978); **21**, 3383 (1980).

[8] S. K. Kuindersma, P. R. Boudewijn, and C. Haas, Phys. Status Solidi B **108**, 187 (1981).

[9] I. Pollini, J. Thomas, and A. Lenselink, Phys. Rev. B **30**, 2140 (1984).

[10] G. Mischler, D. J. Lockwood, and A. Zwick, J. Phys. C **20**, 299 (1987).

[11] S. R. Kuindersma, J. P. Sanchez, and C. Haas, Physica **111B**, 231 (1981).

[12] D. J. Lockwood, G. Mischler, I. W. Johnstone, and M. C. Schmidt, J. Phys. C **12**, 1955 (1979).

[13] C. J. Ballhausen, *Introduction to Ligand Field Theory* (McGraw-Hill, New York, 1962).

[14] M. T. Hutchings, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 227.

[15] B. N. Figgis, *Introduction to Ligand Fields* (Interscience, New York, 1966).

[16] A. J. Freeman and R. E. Watson, Phys. Rev. **120**, 1254 (1960).

[17] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[18] L. M. Falicov, *Group Theory and its Physical Applications* (University of Chicago Press, Chicago, 1966).

[19] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964).

[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 γ_{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 χ is given by the expression

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

for CoI$_2$, and by

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

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.

[22] Y. M. de Haan, in *Molecular Dynamics and Structure of Solids*, edited by R. S. Carter and J. J. Rush, Natl. Bur. Stand. (U.S.) Spec. Publ. No. 301 (U.S. GPO, Washington, D.C., 1969), p. 233.

[23] M. P. Pasternak (private communication).

[24] It should be noted that the second and third levels in Fig. 2(a) cross each other twice at angles very near each other, so that for most of the range of χ the symmetry ordering of the first three levels derived from ${}^4T_{2g}$ remains unchanged: $E(\gamma_{4g})<E(\gamma_{5,6g})<E(\gamma_{4g})$.

[25] I. Pollini, G. Spinolo, and G. Benedek, Phys. Rev. B **22**, 6369 (1980).