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Exciton–Optical-Phonon Coupling in CoF_2

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We present a theory of the temperature dependence of the frequency, linewidth, and infrared absorption strength of the E_g optical phonon in CoF_2, assuming that the coupling between the phonon and the *AD* exciton is responsible for these effects. We find that a model based on the orbit-lattice interaction can account for these phenomena. We also predict that the E_g phonon should be split by application of a magnetic field parallel to the *c* axis. We estimate the "*g* factor" associated with this splitting and find that one should be able to observe the splitting in readily attainable magnetic fields. The temperature dependence of the above phenomena in the paramagnetic and antiferromagnetic state is discussed. A point-charge estimate of the optical-phonon–exciton coupling constant produces a value much smaller than that required to fit the data.

I. INTRODUCTION

The properties of the Co^{++} ion in insulating crystals are most striking. The ground state of this ion (a d^7 configuration) has threefold orbital degeneracy in a cubic crystalline field, while the spin $S=\frac{3}{2}$. The presence of spin-orbit coupling or components of the crystalline field with low symmetry split the twelve-fold degenerate ground-state manifold into a complex of low-lying energy levels. Detailed experimental[1] and theoretical[2] study of Co^{++} placed substitutionally in MgF_2 have been carried out by Gladney. In this environment, the twelve-fold degeneracy of the d^7 ground state is split into six Kramers doublets, with excitation energies that range from 150 to 1400 cm^{-1}.

An approximate description of the electronics excited states of the Co^{++} ion in the antiferromagnet CoF_2 ($T_N = 37.7\,^\circ K$) may be obtained from Gladney's energy level scheme for Co-doped MgF_2. In particular, Martel, Cowley, and Stevenson[3] have studied the low-lying electronic excitations in this compound. These authors find two sets of exciton levels that lie in the 150-cm^{-1} range, for $T > T_N$. The two exciton bands are referred to as the *AC* level and the *AD* level. The *AC* exciton band suffers a Davydov splitting for a general value of the wave vector $\vec{k}$, while symmetry considerations indicate that the Davydov splitting vanishes in the *AD* band,[4] in agreement with the observations.[3]

Allen and Guggenheim[5] have observed infrared (IR) absorption by an optical phonon of E_g symmetry in both the paramagnetic and antiferromagnetic state of CoF_2. The integrated strength of this line was found to exhibit a strong temperature dependence. The width of the line was also strongly temperature dependent, with a minimum at T_N, and a rather large (≈ 6 cm^{-1}) increase in the frequency of the E_g mode was observed as the crystal

was cooled from liquid-nitrogen to liquid-He temperatures. Allen and Guggenheim pointed out that the E_g optical phonon, which has no first-order electric dipole moment, can become IR active by mixing with a magnetic dipole active exciton level. These authors found that they could account well for the temperature dependence of the integrated absorption strength by invoking this mechanism, although no detailed discussion of the nature of the exciton–optical-phonon coupling is presented in their work.

In this paper we present a theory of the contribution to the linewidth and frequency shift of the E_g phonon from the exciton-phonon coupling. The single-ion-orbit–lattice interaction is assumed to be the dominant source of exciton-phonon coupling. We presume that at low temperatures the major contribution to these quantities comes from the linear coupling between the E_g phonon and the lifetime broadened exciton level. We also derive an expression for the integrated strength of the IR absorption line of the E_g phonon in terms of the parameters of our mode. A consistent interpretation of all these phenomena can be obtained with an appropriate choice of the exciton-E_g-phonon coupling constant.

We also point out that the twofold degenerate E_g optical phonon may be split by application of a magnetic field along the c axis of the crystal; the splitting is linear in the magnetic field, and has the character of the Zeeman effect. We find the effective g factor of the E_g phonon is a decreasing function of temperature, with a value the order of 0.6 at $T=0$. Observation of this splitting thus should be feasible either by IR or Raman studies in attainable magnetic fields.

II. THEORY OF INFRARED ABSORPTION IN CoF_2

In this section, we introduce a model Hamiltonian that describes the linear coupling between the E_g optical phonon and the AD exciton level. We assume that the single-ion-orbit–lattice interaction gives the dominant contribution to this interaction. Furthermore, since the excitation energy of the AD exciton lies in the range of 150–190 cm^{-1}, and the frequency of the E_g phonon is ≈ 250 cm^{-1}, these levels may be expected to mix strongly even if the coupling is weak. Since the second excited state of the Co^{++} ion in this crystal field is roughly 800 cm^{-1} above the ground state,[2] it should be a good approximation to confine our attention only to the coupling between the phonon and the AD exciton. (Symmetry considerations show that the AC exciton is forbidden to couple to the E_g phonon via the first-order orbit-lattice mechanism.)

In the paramagnetic state, the E_g phonon is twofold degenerate. In the antiferromagnetic (AF) state, the E_g representation decomposes according to the rule $E_g = \Gamma_3^+ + \Gamma_4^+$, where Γ_3^+ and Γ_4^+ are the one-dimensional irreducible representations of the unitary subgroup (D_{2h}). With time-reversal symmetry, Γ_3^+ and Γ_4^+ are degenerate.[4] Let Q_3 and Q_4 denote the normal coordinates associated with the Γ_3^+ and Γ_4^+ optical phonons at $\vec{k}=0$.

There are two inequivalent Co^{++} sites in the crystallographic unit cell of CoF_2. We refer to the sites as the A site and the B site, respectively. Loudon has demonstrated that symmetry considerations require the Davydov splitting of the AD exciton to vanish.[4] The level is thus twofold degenerate, in the absence of a magnetic field. Furthermore, in the limit when the exciton bandwidth is small compared to the excitation energy, one finds that one of the AD excitons is entirely associated with the A sublattice, and one with the B sublattice of Co^{++} ions.[4] We let $|E_{A,B}\rangle$ and $|G_{A,B}\rangle$ be the excited and ground electronic states of the A, B sublattice from which the AD excitons are constructed. One may verify that the transition operator (we use Loudon's notation[4]) $|E_A\rangle\langle G_A| + |E_B\rangle\langle G_B|$ transforms like the Γ_3^+ representation of the unitary point group, while $|E_A\rangle\langle G_A| - |E_B\rangle\langle G_B|$ transforms like Γ_4^+. Thus, assuming that the single-ion-orbit–lattice interaction is the dominant source of mixing between the $\vec{k}=0$ E_g optical phonons and the $\vec{k}=0$ AD excitons, the coupling term has the form

$$H_{x-p} = \omega_0^{3/2} G[Q_3 + Q_4)|E_A\rangle\langle G_A| + (Q_3 - Q_4)|E_B\rangle\langle G_B|] + \text{H. c.} \qquad (1)$$

In Eq. (1), ω_0 is the frequency of the E_g phonon, and G is a coupling constant. Our choice of Q_3 and Q_4 will be such that G is dimensionless. (We use units with $\hbar = 1$.) The form in Eq. (1) assumes no magnetic field is present. While we could work directly with Eq. (1), we find it convenient to replace the transition operators $|E_A\rangle\langle G_A|$, $|E_B\rangle\langle G_B|$ by the spin-$\frac{1}{2}$ operators $s_A^{(-)}$, $s_B^{(-)}$.[6]

We add to the coupling term of Eq. (2) the Hamiltonian of the bare phonon and exciton levels:

$$H_p = \tfrac{1}{2}(P_3^2 + P_4^2) + \tfrac{1}{2}\omega_0^2(Q_3^2 + Q_4^2),$$

$$H_x = -\omega_A s_A^z - \omega_B s_B^z. \qquad (2)$$

In the absence of a magnetic field, $\omega_A = \omega_B \equiv \omega_x$. We allow for the presence of a magnetic field by assuming ω_A differs from ω_B. We presume the principal effect of the magnetic field H is to induce a Zeeman splitting of the twofold degenerate AD exciton. We ignore the effect of the magnetic field on H_{x-p}. This approximation is reasonable because of the near resonance between ω_0 and ω_x.

To describe the IR absorption via the magnetic dipole interaction, we consider the interaction of the magnetic field h_1 of the IR radiation with the

exciton. This coupling may be described by adding to the Hamiltonian the term

$$H_{IR} = \mu_0 g_T h_1 e^{-i\Omega t}[s_A^{(-)} + s_B^{(-)} + s_A^{(+)} + s_B^{(+)}] + \text{H. c.} \ , \tag{3}$$

where

$$\mu_0 = e\hbar/2mc \text{ and } g_T = \langle E_A | L_x + 2S_x | G_A \rangle \ .$$

We calculate the IR absorption coefficient by first computing the rate at which energy is absorbed by the system, then converting this expression to an absorption length. We find that the energy per unit time absorbed by the system in the presence of H_{IR} is given by

$$dE/dt = 2\Omega \ \mu_0^2 g_T^2 h_1^2 N \ \text{Im} \ g(-\Omega - i\eta) \ , \tag{4}$$

where N is the number of unit cells in the crystal,

$$g(\Omega) = i\int_0^\infty dt \, e^{-i\Omega t}\langle [S(0), \ S(t)]\rangle ,$$

with

$$S(t) = s_A^{(+)}(t) + s_A^{(-)}(t) + s_B^{(+)}(t) + s_B^{(-)}(t) \ .$$

Next we need the form of $g(\Omega)$. We find the form of this function by using an equation of motion method and a simple decoupling scheme. Consider the functions $G_{A,B}^{\pm}(t) = i\theta(t)\langle [S(0), s_{A,B}^{\pm}(t)]\rangle$. We find

$$\left(i\frac{\partial}{\partial t} - \omega_A\right) G_A^+(t) = 2\langle s_A^z\rangle \delta(t)$$

$$+ 2i\omega_0^{3/2} G\theta(t)\left(\langle\{S(0), s_A^z(t)[Q_3(t) + Q_4(t)]\}\rangle\right) \ . \tag{5}$$

We decouple the equation by replacing $\langle [S(0), s_A^z(t) Q_{3,4}(t)]\rangle$ by $\langle s_A^z\rangle\langle [S(0), Q_{3,4}(t)]\rangle$. Then if we define

$$s_{3,4}(t) = i\theta(t)\langle [S(0), Q_{3,4}(t)]\rangle ,$$

the equation of motion for $\partial^2 s_{3,4}/\partial t^2$ involves only the functions $s_{3,4}(t)$, and the original correlation functions $G_{A,B}^{\pm}(t)$. Upon taking the Fourier transforms of these equations with respect to time, we obtain simple linear algebraic equations for $G_{A,B}^{\pm}(\Omega)$ and $\delta_{3,4}(\Omega)$. Upon solving these equations, and noting that $g(\Omega) = G_A^+(\Omega) + G_A^-(\Omega) + G_B^+(\Omega) + G_B^-(\Omega)$, we have

$$g(\Omega) = \sum_{i=A,B} \frac{4\omega_i(\omega^2 - \omega_0^2)\langle s_i^z\rangle - 8\omega_0^3(G - G^*)^2\langle s_i^z\rangle^2}{(\omega^2 - \omega_0^2)(\omega^2 - \omega_i^2) - 8\omega_0^3\omega_i|G|^2\langle s_i^z\rangle} \ . \tag{6}$$

In the result of Eq. (6), the quantity $\langle s_i^z\rangle = \frac{1}{2}\tanh(\omega_i/2k_BT)$.[7] In order to explore the properties of $g(\Omega)$, it is convenient to first assume no magnetic field is present, and then examine the effect of applying a field.

(i) The case of zero dc magnetic field: We set $\omega_A = \omega_B = \omega_x$, and $\langle s_A^z\rangle = \langle s_B^z\rangle = \langle s^z\rangle$. Then we may write

$$g(\Omega) = \frac{4\omega_x(\omega^2 - \omega_0^2)\langle s^z\rangle - 8\omega_0^3(G - G^*)^2\langle s^z\rangle^2}{(\omega^2 - \tilde{\omega}_0^2)(\omega^2 - \tilde{\omega}_x^2)} ,$$

where $\tilde{\omega}_0$ and $\tilde{\omega}_x$ are renormalized optical-phonon and exciton frequencies. For small values of $|G|$, one has

$$\tilde{\omega}_0 = \omega_0 + 4\omega_0^2\omega_x|G|^2\langle s^z\rangle/(\omega_0^2 - \omega_x^2) \ , \tag{7a}$$

$$\tilde{\omega}_x = \omega_x - 4\omega_0^3|G|^2\langle s^z\rangle/(\omega_0^2 - \omega_x^2) \ . \tag{7b}$$

One may easily find expressions for $\tilde{\omega}_0$ and $\tilde{\omega}_x$ from the zeros of $G(\Omega)$ without restricting $|G|$ to the limit $|G| \ll 1$, but Eqs. (7a) and (7b) will suffice for our purposes.

Since infrared absorption occurs at those frequencies for which $g(\Omega)$ has poles, the presence of the coupling between the E_g optical phonon and the AD exciton gives rise to a shift in the phonon frequency and the exciton frequency. It is the former shift that will concern us in this work, since the exciton frequency is strongly temperature dependent by virtue of the exchange field associated with the AF state. It would thus be difficult to experimentally separate the shift exhibited in Eq. (7b) from that due to the exchange field.

The frequency shift of the phonon [Eq. (7a)] will exhibit a strong temperature dependence because ω_x is near ω_0, and ω_x is also strongly temperature dependent below the Néel point by virtue of the effect of the exchange field. Equation (7a) predicts that the phonon frequency should decrease with temperature for $T < T_N$, since ω_x moves farther from ω_0 in this region.[3] We present estimates of the magnitude of the frequency shift and a plot of its temperature dependence in Sec. III.

Until this point, we have treated the exciton level as a completely sharp excitation with zero width. In fact, for $T \lesssim T_N$, the neutron studies indicate the AD transition has a considerable width the order of 30 cm^{-1}.[3] This means that the optical phonon can be damped by the direct coupling to the exciton since ω_0 lies in the "wing" of the exciton line. One may calculate the contribution to the width of the optical-phonon line from this source by replacing ω_x in the denominator of Eq. (7a) by $\omega_x + \frac{1}{2}i\Gamma_x$, where Γ_x is the full width at half-maximum of the exciton line. The quantity $\tilde{\omega}_0$ acquires a nonzero width. The full width at half-maximum Γ_{ph} of the exciton-induced absorption line is found from Eq. (7a) to be

$$\Gamma_{ph} = [8\omega_0^2\omega_x^2|G|^2\langle s^z\rangle/(\omega_0^2 - \omega_x^2)^2]\Gamma_x \ , \tag{8}$$

when $(\omega_0 - \omega_x) \gg \frac{1}{2}\Gamma_x$. The temperature dependence of the linewidth of the E_g optical phonon observed by Allen and Guggenheim can be accounted for by the expression given in Eq. (8). Martel *et al.*[3] find that the width Γ_x of the AD exciton level is insensitive to T for $T < T_N$, but increases sharply as T passes through T_N. Below T_N, the temperature dependence of Γ_{ph} is dominated by the fact that ω_x moves away from ω_0 as T increases. Thus, for $T < T_N$, Γ_{ph} decreases with increasing temperature.

As T increases through T_N, ω_x becomes temperature independent, but now the exciton level becomes broader (Γ_x increases). Thus, for $T > T_N$, Γ_{ph} increases; the phonon linewidth thus passes through a minimum near T_N. This is precisely the behavior observed for Γ_{ph}.[5] It must be realized that superimposed upon the exciton-induced linewidth, one also has an anharmonic contribution. This latter contribution should not be strongly dependent on temperature when T is the order of T_N, however. In Sec. III, we present an estimate of the magnitude of the contribution to Γ_{ph} given in Eq. (8), and a graph of its temperature dependence will be displayed.

Finally, we compute the integrated strength of the IR absorption. For this purpose, we may ignore the lifetime effects discussed above. For $|G| \ll 1$, we find

$$\mathrm{Im}[g(-\Omega - i\eta)] = 4\pi\delta(\Omega - \tilde{\omega}_x) + \frac{8\pi\omega_0^2(\omega_x^2\cos^2\varphi + \omega_0^2\sin^2\varphi)}{(\omega_0^2 - \omega_x^2)^2} \times |G|^2 \tanh^2\left(\frac{\omega_0}{2k_BT}\right)\delta(\Omega - \tilde{\omega}_0), \quad (9)$$

where we write $G = |G|e^{i\varphi}$. The attenuation constant $\alpha(\Omega)$ for the radiation in the crystal may be found by inserting Eq. (9) into Eq. (4), dividing by the energy $Vh_1^2/2\pi$ of the radiation stored in the crystal [we have used a convention where $h(t) = 2h_1\cos\Omega t$], and then dividing by $\bar{c} = c/\epsilon^{1/2}$ to obtain the attenuation constant in cm^{-1}. For Ω near $\tilde{\omega}_0$, we have

$$\alpha(\Omega) = 32\pi^2\mu_0^2 g_T^2 \epsilon^{1/2} \frac{\omega_0^2(\omega_x^2\cos^2\varphi + \omega_0^2\sin^2\varphi)}{V_c c(\omega_0^2 - \omega_x^2)^2} \times |G|^2 \tanh^2\left(\frac{\omega_0}{2k_BT}\right)\delta(\Omega - \tilde{\omega}_0). \quad (10)$$

In this expression V_c is the volume of the unit cell. Allen and Guggenheim plot the integrated intensity $I = \int d(1/\lambda)\,\alpha(\Omega)$ as a function of temperature. From Eq. (10),

$$I = 16\pi\mu_0^2 g_T^2 \epsilon^{1/2} \frac{\omega_0^3(\omega_x^2\cos^2\varphi + \omega_0^2\sin^2\varphi)}{\hbar V_c c(\omega_0^2 - \omega_x^2)^2} \times |G|^2 \tanh^2\left(\frac{\omega_0}{2k_BT}\right). \quad (11)$$

The temperature dependence of I in Eq. (11) is very similar to that obtained by Allen and Guggenheim.[5] These authors compared the predicted tempearature dependence with the experiment in their work. We shall estimate the strength of I in Sec. III, after a value of $|G|^2$ is obtained from the linewidth data.

(ii) The effect of a nonzero magnetic field: In the presence of a magnetic field, $\omega_A \neq \omega_B$. In fact, if g_0 is the g factor of the ground electronic state $|G\rangle$, and g_1 is that for the excited state $|E\rangle$, then for the AD exciton,

$$\omega_A - \omega_B = \mu_0(g_0 + g_1)H,$$

where H is the strength of the magnetic field. We assume H is applied parallel to the c axis of the crystal. When $H \neq 0$, two distinct poles near $\tilde{\omega}_0$ appear in the Green's function of Eq. (6). If we denote the position of the poles by $\tilde{\omega}_0(+)$ and $\tilde{\omega}_0(-)$, we define a Landé g factor for the phonon by writing $\tilde{\omega}_0(+) - \tilde{\omega}_0(-) = \mu_0 g_{ph} H$ for small H. Then

$$g_{ph} = \frac{2\omega_0^2\omega_x^2|G|^2}{(\omega_0^2 - \omega_x^2)^2}\tanh\left(\frac{\omega_x}{2k_BT}\right) \times \left[1 + \frac{\omega_0^2}{\omega_x^2} + \frac{(\omega_0^2 - \omega_x^2)}{k_BT\omega_x}\ \mathrm{csch}\left(\frac{\omega_x}{k_BT}\right)\right](g_0 + g_1). \quad (12)$$

Thus, the doubly degenerate optical phonon is split by the presence of a magnetic field. Note that the splitting exists even in the paramagnetic state. We shall estimate the magnitude of g_{ph} in Sec. III.

III. COMPARISON BETWEEN THEORY AND EXPERIMENT

In this section, we consider the comparison between the theory of Sec. II and the observations of Allen and Guggenheim. We also estimate the value of the Landé g factor g_{ph} given in Eq. (12).

First, consider the linewidth Γ_{ph} of the E_g mode given by our model [Eq. (8)]. In Fig. 1, the solid curve is a plot of $\Gamma_{ph}(T)/\Gamma_{ph}(0)$ for $T \lesssim T_N$. For $T < T_N$, $\Gamma_x(T)$ appears insensitive to temperature, to judge from the neutron data of Martel *et al.*,[3] if we presume that the width of the $\vec{k} = 0$ exciton level

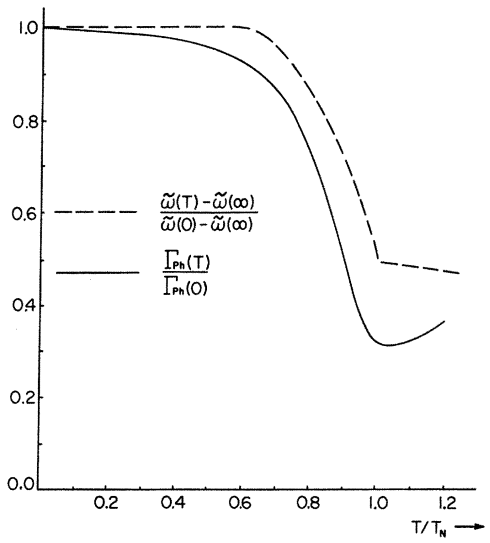

FIG. 1. Temperature dependence of the phonon frequency and linewidth. Both quantities have been normalized to approach a value of unity as $T \to 0$.

is similar to the width of the finite $\vec{k}$ modes studied by these authors. Indeed, for $T < T_N$, the linewidth appears insensitive to the value of $\vec{k}$. In all cases studied, $\Gamma_x(T)$ rises sharply near T_N, and the behavior of this quantity appears wave-vector dependent above T_N. As a consequence, we terminate our calculated curbes at $1.2\,T_N$. The striking feature of the solid curve of Fig. 1 is the rapid falloff of $\Gamma_{ph}(T)$ with increasing T, and the minimum near T_N. Allen and Guggenheim find $\Gamma_{ph}(T_N)/\Gamma_{ph}(0) \approx 0.4$, while our model predicts the ratio ≈ 0.3. This suggests the presence of an anharmonic contribution $\Gamma_{ph}^{(A)}$ to Γ_{ph}, with $\Gamma_{ph}^{(A)} \approx 0.5\ \mathrm{cm}^{-1}$ at T_N. Because of our uncertainty concerning the behavior of $\Gamma_x(T)$ for T much greater than T_N, and the fact that $\Gamma_{ph}^{(A)}$ increases with T, it is difficult to make a precise comparison between theory and experiment for $T > 1.2\,T_N$ at this time. Nonetheless, we feel that the linear coupling between the E_g optical mode and the lifetime broadened exciton level accounts for a large portion of the observed linewidth Γ_{ph} below liquid-nitrogen temperatures.

At $T = 0$, the neutron data indicates $\Gamma_x \cong 33\ \mathrm{cm}^{-1}$.[3] Also $\omega_x(T=0) \cong 195\ \mathrm{cm}^{-1}$ and $\omega_0 = 256\ \mathrm{cm}^{-1}$ at helium temperatures. Thus, we estimate from Eq. (8) $\Gamma_{ph}(T=0) \cong 470\,|G|^2\ \mathrm{cm}^{-1}$. If we presume that all the linewidth observed at $T = 0$ ($4\ \mathrm{cm}^{-1}$) has its origin in the exciton-phonon coupling, then $|G| \approx 0.092$.

Next consider the frequency shift of the optical mode. In Fig. (1), we plot $\delta\omega(0)$ (dashed line). Since no detailed studies of $\delta\omega(T)$ have been reported, we cannot compare the quantity with experiment. We have

$$\tilde{\omega}_0(T=\infty) - \tilde{\omega}_0(T=0) = 2\omega_0^2\omega_x|G|^2/(\omega_0^2 - \omega_x^2)\ ,$$

where the right-hand side is evaluated at $T = 0$. For the parameters given above, we find

$$\tilde{\omega}_0(T=\infty) - \tilde{\omega}_0(T=0) \cong 8\ \mathrm{cm}^{-1}\ .$$

Allen and Guggenheim report $\tilde{\omega}_0\,(4.2\,^\circ\mathrm{K}) = 256\ \mathrm{cm}^{-1}$, and a recent room-temperature Raman study[8] yields $\tilde{\omega}_0\,(300\,^\circ\mathrm{K}) = 246\ \mathrm{cm}^{-1}$. The above estimate suggests that about $8\ \mathrm{cm}^{-1}$ of the 10-cm^{-1} difference between the room-temperature and liquid-helium temperature frequency $\tilde{\omega}_0$ can be accounted for as a consequence of the exciton-phonon coupling.

Note that we predict a discontinuity in slope of the quantity $\delta\omega(T)$ at $T = T_N$. It would be useful to make a more extensive study of the temperature dependence of $\tilde{\omega}_0$, since the importance of the exciton contribution to $\delta\omega$ could be clearly established by observation of the slope discontinuity.

Next consider the integrated strength of the IR absorption line [Eq. (11)]. Allen and Guggenheim have demonstrated that the form in Eq. (11) gives an excellent account of the observed temperature dependence. For CoF_2, $V_c \cong 70\ \text{Å}^3$, and we use $\epsilon_0 = 1.5$ for the dielectric constant. This is the value appropriate for the ordinary ray in CoF_2 at $256\ \mathrm{cm}^{-1}$, as determined from the data of Balkanski *et al.*[9] We have estimated g_T from Gladney's wave functions, and we find $g_T \cong 2.3$. Then from Eq. (11), we find

$$I(T \cong 0) = 6.7\times10^4(1 + 0.72\sin^2\varphi)|G|^2\ \mathrm{cm}^{-2}\ .$$

Allen and Guggenheim[5] find $I(T=0) = 425\ \mathrm{cm}^{-2}$. This requires $(1 + 0.72\sin^2\varphi)^{1/2}|G| = 0.08$. While we have no information about the phase angle φ, it is clear that the strength of the exciton-induced IR absorption at $\tilde{\omega}_0$ is consistent with a value of $|G|$ quite close to that deduced from the linewidth and frequency shift data. Indeed, if $\varphi = 0$ (G is real), then from the IR absorption strength, we obtain a value of G within 15% of the value deduced from the values of $\Gamma_{ph}(T)$ and $\delta\omega(T)$.

We should note that the absorption at $256\ \mathrm{cm}^{-1}$ lies quite near the frequency of an IR-active E_u phonon at $268\ \mathrm{cm}^{-1}$.[9] Thus, there is liable to be some uncertainty in the experimental determination of the absolute value of I. Furthermore, our estimate of I requires knowledge of g_T. We have calculated this quantity for the case of a Co impurity placed substitutionally in MgF_2.[2] Thus, our estimate of g_T is liable to be somewhat in error, particularly in the light of the concluding remarks of the present section.

Thus, we conclude that the present model is able to give an adequate quantitative account of the data of Allen and Guggenheim, and Macfarlane and Ushioda on the magnitude and temperature dependence of $\delta\omega(T)$, $\Gamma_{ph}(T)$, and $I(T)$ for a single choice of the exciton–optical-phonon coupling constant $|G|$. Let us now turn to the Landé g factor [Eq. (12)] associated with E_g optical phonon. As $T \to 0$, from Eq. (12),

$$g_{ph}(T=0) = \frac{2\omega_0^2(\omega_0^2 + \omega_x^2)|G|^2}{(\omega_0^2 - \omega_x^2)^2}\,(g_0 + g_1)\ .$$

With $\omega_0 = 256\ \mathrm{cm}^{-1}$, $\omega_x = 195\ \mathrm{cm}^{-1}$, $|G| = 0.092$, and $g_0 = g_1 = 2$, we find

$$g_{ph} \cong 0.6\ .$$

The Landé g factor associated with the E_g phonon is thus quite large. This is a consequence of the close proximity of the optical phonon to the exciton level. For a g factor of this magnitude, application of a 50-kG field produces a splitting of the E_g mode the order of $1.5\ \mathrm{cm}^{-1}$. Since this splitting is comparable to the linewidth Γ_{ph} ($\approx 4\ \mathrm{cm}^{-1}$) at $T = 0$, the effect of the splitting should be observable. A higher field, say 100 kG, should produce a resolvable doublet. Observation of this large phonon g factor would provide strong evidence that the model employed in this work gives a complete description of the properties of the E_g optical mode in CoF_2.

We have attempted to estimate the value of G by employing Gladney's wave functions,[2] combined with a nearest-neighbor point-charge model of the crystal field, and the assumption that in CoF_2 the electronic excitations associated with the Co^{++} ion can be treated as completely localized to the Co site. As remarked earlier, this calculation produces a value of $|G|$ some six or seven times smaller than the value 0.09 estimated from the experimental data. Before our work, Moriya and coworkers also found a value of $|G|$ far smaller than that required to fit the data, on the basis of a similar computation.[10] Thus, it appears as if one cannot apply Gladney's wave function for Co-doped MgF_2 directly to CoF_2 without modification. Since our crystal-field calculation is long and tedious, but employs only well-known straightforward techniques, we omit the details of the calculation from the present note.

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COMMENTS AND ADDENDA

The Comments and Addenda section is for short communications which are not of such urgency as to justify publication in Physical Review Letters and are not appropriate for regular Articles. It includes only the following types of communications: (1) comments on papers previously published in The Physical Review or Physical Review Letters; (2) addenda to papers previously published in The Physical Review or Physical Review Letters, in which the additional information can be presented without the need for writing a complete article. Manuscripts intended for this section may be accompanied by a brief abstract for information-retrieval purposes. Accepted manuscripts will follow the same publication schedule as articles in this journal, and galleys will be sent to authors.

Comment on Determination of Nuclear Quadrupole Interactions: Copper-Doped Rutile*

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A complete diagonalization of the spin Hamiltonian is necessary to obtain consistent principal values of the nuclear quadrupole coupling tensor from $\Delta M_I = 0$ and $\Delta M_I = \pm 2$ lines in EPR spectra. As an example, proper recalculation for $TiO_2 : Cu^{++}$ shows greatly revised values, $Q' \approx 0.0010$ cm^{-1}, $\eta \approx 0.1$.

In the extraction of quadrupole coupling constants for Cu^{++} and other paramagnetic ions from orientation-dependent allowed and forbidden hyperfine transitions,[1] we have been struck by the inadequacies of the second-order perturbation expressions for positions of certain of the lines in some ranges of orientation of the magnetic field.[2] As Lyons and Kedzie[3] have already demonstrated, the perturbation expressions are inadequate for the forbidden hyperfine lines with $\Delta M_I = \pm 1$ when the magnetic field lies between the principal axis and its perpendicular. Here we point out that even for magnetic field perpendicular to the principal axis of a uniaxial or near-uniaxial site, the perturbation-theory