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COMMENTS AND ADDENDA

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Microscopic Description of Magnon–Optical-Phonon Interaction in $FeCl_2 \cdot 2H_2O$

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A simple physical mechanism is described for the magnon–optical-phonon interaction observed in $FeCl_2 \cdot 2H_2O$: A vibration of the waters of hydration gives rise to a modulating Coulomb potential at the Fe^{2+} site; this potential acts on the orbital part of the Fe^{2+} wave function and is coupled to the spin via the spin-orbit coupling. The calculated magnitude (~ 1.2 cm^{-1}) of the interaction is in remarkably good agreement with the experimental value of 1.3 cm^{-1}.

The interaction between magons and *long-wavelength acoustic* phonons gives rise to a wide variety of magnetoelastic phenomena, which have been studied extensively by microwave and ultrasonic techniques.[1] However, there have been only a few observations of magnon-phonon interactions involving either *short-wavelength* (high-*k*) phonons[2] or *optical* phonons.[3-6] Using inelastic neutron diffraction, Dolling and Cowley[2] have observed a level anticrossing (as a function of *k*) of a magnon and a short-wavelength acoustic phonon in antiferromagnetic UO_2. In CoF_2, effects of the magnon-phonon interaction on both magnons and optical phonons have been observed in far-infrared[3] and Raman[4] experiments. But perhaps the simplest magnon–optical-phonon interaction to analyze is that observed in the far-infrared experiments of Hay and Torrance.[5] As a function of applied magnetic field, magnons and optical phonons are observed to interact strongly in the antiferromagnetic, ferrimagnetic *and* ferromagnetic phases of $FeCl_2 \cdot 2H_2O$. In a similar material, $CoCl_2 \cdot 2H_2O$, Torrance and Tinkham[6] have observed similar effects, but as in CoF_2 the magnetic excitation spectrum is more complex. Unfortunately, a satisfactory theoretical description of this interaction and its magnitude has been given only for UO_2.[2] In this paper[7] we develop a simple microscopic description of the origin of the magnon–optical-phonon interaction in $FeCl_2 \cdot 2H_2O$.

Magnon-phonon interactions generally arise from the modulation by lattice vibrations of one or more of the following interactions: (i) the dipole-dipole interaction, (ii) the exchange interaction (although only the anisotropic part gives rise to a first-order interaction), and (iii) the crystal field at the spin site. This modulating field may be felt by the orbital angular momentum and transferred to the spin via the spin-orbit coupling.

Considering a given material and a given mechanism, the phonons with higher energies will give rise to a greater modulation of one of the above interactions, since these phonons generally have larger relative displacements of neighboring ions. Therefore, we expect optical and short-wavelength acoustical phonons to *generally* interact more strongly with magnons than the more familiar long-wavelength acoustic phonons. For the former phonons, the interaction energies (~ 1–10 cm^{-1}) are in fact much larger than typical long-wavelength acoustic interactions ($\sim 10^{-4}$–10^{-1} cm^{-1}).

Below its Néel temperature of 23 °K, $FeCl_2 \cdot 2H_2O$ is metamagnetic.[8] For low magnetic fields, H_0, applied along the easy axis (z), the Fe^{2+} spins order antiferromagnetically (AF). At $H_0 = H_{C1} = 35$ kOe, there is a discontinuous transition to a ferrimagnetic phase. At $H_0 = H_{C2} = 45$ kOe there is a second metamagnetic transition to a ferromagnetic state, with all the Fe^{2+} spins aligned along the field. Far-infrared-absorption results for all three phases are summarized in Fig. 1: The dots represent the observed absorption frequencies.[5] The heavy solid

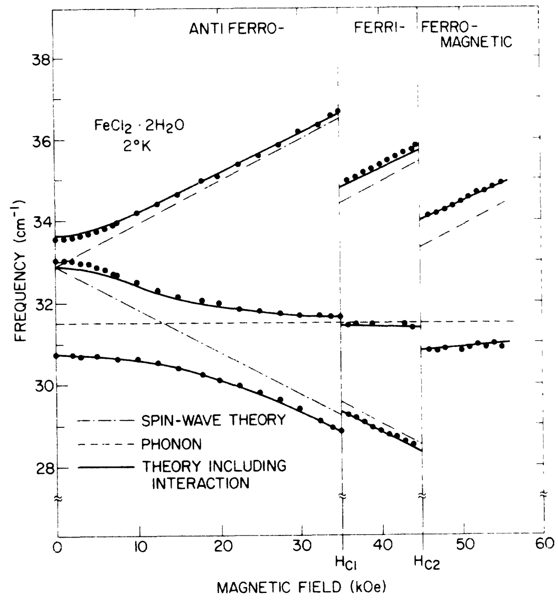

FIG. 1. Absorption frequencies in $FeCl_2 \cdot 2H_2O$.

curves in Fig. 1 are the theoretical fit, which was obtained[5] by assuming that the calculated spin-wave excitations (dash-dot lines in Fig. 1) interact with a phonon at 31.5 cm^{-1} (dashed line). In the ferromagnetic region the phenomenological magnon-phonon coupling energy necessary to best fit the data is 1.3 ± 0.1 cm^{-1}. The value necessary in the AF region is empirically $\sim 1/\sqrt{2}$ times as large. Furthermore, intensity measurements[9] showed that this was a normally infrared *inactive* phonon, presumably an optical phonon with $k = 0$.

In order to obtain a microscopic description of the magnon-phonon interaction in $FeCl_2 \cdot 2H_2O$, we first consider which of the phonons may be involved. Since we are looking for a $k = 0$, optical phonon, we need only consider the relative vibrations of atoms within the $FeCl_2 \cdot 2H_2O$ unit cell, which is schematically shown in Fig. 2. The vibrational frequencies associated with the strong bonds between Fe^{2+} and Cl^- ions are surely much higher than the observed 31.5 cm^{-1} (which is particularly low for an optical-phonon frequency). For simplicity we therefore regard the Fe^{2+} and Cl^{-1} ions as stationary and consider the possible phonon modes associated with the weakly bonded waters of hydration, which might be expected to have very low frequencies. In fact, very recently Nicoli and Tinkham[10] have shown that the frequency of the corresponding phonon[6] in $CoCl_2 \cdot 2H_2O$ shifts downward upon deuteration by 5%. This is the amount of shift expected if the phonon is dominated by the rigid motion of the waters of hydration. For this reason, we neglect the internal vibrations and rotations of the water molecules.

In order to find the mechanism for the magnon–optical-phonon coupling in $FeCl_2 \cdot 2H_2O$, we first recognize that vibrations of the water molecules do not modulate the dipole-dipole interaction [mechanism (i) above]. Furthermore, the exchange paths between Fe^{2+} spins probably do not involve the waters of hydration [mechanism (ii)]. However, the vibrational modes of the water molecules can modulate the crystal field at the Fe^{2+} site [mechanism (iii)], giving rise to the observed interaction $FeCl_2 \cdot 2H_2O$. Therefore, only even-parity displacements of the waters need be considered. There are three such modes, which are shown schematically in Fig. 2 and labeled A, B, and C. For these modes the displacements are directed along the y, x, and z axes, respectively.[11]

The Coulomb potential $V(r)$ at an Fe^{2+} site is principally modulated by the displacement of the point charges on the nearest-neighbor waters of hydration. The first term in the expansion is shown in Fig. 2. Note that each mode contributes, but that each contribution has a different dependence on the position, x, y, z, of the d electron. In this figure u is the displacement of the water molecules and Z' is the magnitude of the equivalent point charge, which is related to the dipole moment.[12]

The ground state of a free Fe^{2+} ion is ^5D, which is split by the octahedral component of the crystal field into an orbital triplet, $^5T_{2g}$, which lies $\Delta \sim 10^4$ cm^{-1} below an orbital doublet ^5E_g. The energies of the $^5T_{2g}$ wave functions $|xz\rangle$, $|xy\rangle$, and $|yz\rangle$ are then split by the rhombic part of the crystal field, leaving $|xz\rangle$ lowest.[9,13] (We adopt the convention that $|xy\rangle$ is xy times a real, positive, radial function,[11] etc.) Neglecting all states not belonging to the ^5D manifold, we express the potential in terms of the d-electron orbital-angular-momentum operators, L_x, L_y, L_z, since these are easier to work with than

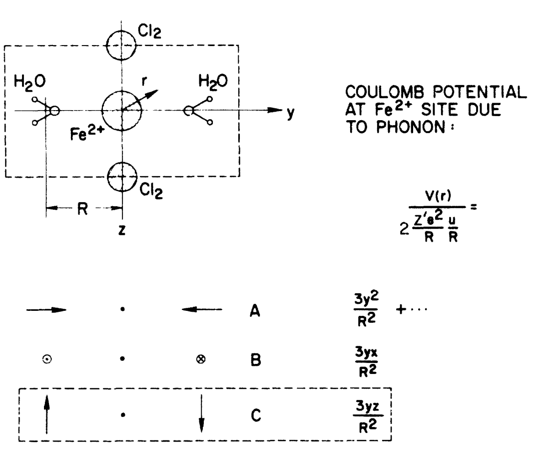

FIG. 2. Schematic diagram of the vibrational modes of the waters of hydration, neglecting the small distortion from local octahedral symmetry.

the coordinates. We now consider a perturbing Hamiltonian containing the spin-orbit coupling and a *general* quadratic potential:

$$\mathcal{H} = \lambda \vec{L}\cdot\vec{S} + \sum_{i,j} t_{ij} L_i L_j \quad , \tag{1}$$

where the coefficients t_{ij} are proportional to the phonon amplitude u.

We use the perturbation procedure of Abragam and Pryce[14] to calculate the effect of Eq. (1) on the ground state and express the result in the form of a spin Hamiltonian:

$$\mathcal{H}_{\text{spin}} = -DS_z^2 - E(S_x^2 - S_y^2) + \mathcal{H}_{\text{m-ph}} \quad , \tag{2}$$

where z is the axis of magnetization. The spin-orbit coupling gives rise to the magnetic anisotropy parameters D and E: $D = \lambda^2(1/\Delta_z - 1/2\Delta_x - 2/\Delta)$ and $E = \lambda^2(1/2\Delta_x - 2/\Delta)$. Here Δ_x and Δ_z are the energies of $|xy\rangle$ and $|zy\rangle$ with respect to the ground state $|xz\rangle$, and Δ is the T_{2g}-E_g splitting. Neglecting the effect of the ${}^5E_g$ level, we find the leading term in the magnon-phonon coupling,

$$\mathcal{H}_{\text{m-ph}} = 3\lambda^2\left(\frac{1}{\Delta_x\Delta_z}\left[t_{xy}(S_xS_y + S_yS_x) + t_{xz}(S_xS_z + S_zS_x) + t_{yz}(S_yS_z + S_zS_y)\right] + \frac{1}{\Delta_x^2}(t_{zz} - t_{yy})S_x^2 + \frac{1}{\Delta_z^2}(t_{xx} - t_{yy})S_z^2\right). \tag{3}$$

Thus, several types of coupling between magnons and phonons arise. For example, mode A (which transforms like y^2 and hence t_{yy}) modulates the single-ion anisotropy energy, as seen from Eqs. (2) and (3). Similarly, mode B (which transforms like xy and hence t_{xy}) gives rise to a term containing S_xS_y and hence couples one phonon to two magnons.[15] The coupling between one magnon and one phonon is caused by the t_{xz} and t_{yz} terms.[15] In our case there is no phonon transforming like xz, but mode C does transform like yz. Therefore, it must be the phonon (C) polarized along the axis of magnetization (z), which is observed to interact with the magnons in $FeCl_2 \cdot 2H_2O$.[16]

A crude picture of how the motion of the water molecules is coupled to the Fe^{2+} spins is as follows: The wave function ($|xz\rangle$) of the Fe^{2+} ion has lobes in the xz plane. The vibration of the water molecules along z causes the Fe^{2+} lobes to wobble slightly about the x axis. This wobbling gives rise to a wobbling of the spin due to the spin-orbit coupling.

We may now relate t_{yz} of Eqs. (1) and (3) to the modulated Coulomb potential due to mode C (Fig. 2) and express the phonon displacement u and S_y and S_z in terms of the creation operators, $c_k^\dagger$ and $a_k^\dagger$, and annihilation operators, c_k and a_k, for phonons and magnons, respectively. For the ferromagnetic phase, we sum Eq. (3) over the lattice and obtain

$$\mathcal{H}'_{\text{m-ph}} = \sum_k \frac{\lambda^2}{\Delta_x\Delta_z}\,\frac{Z'e^2}{R}\,\frac{3\langle r^2\rangle}{7R^2}\left(\frac{2S-1}{R}\right) \times\left(\frac{\hbar S}{2m\omega_k}\right)^{1/2}(c_k^\dagger a_k + c_k a_k^\dagger) \; , \tag{4}$$

neglecting terms proportional to $c_k^\dagger a_{-k}^\dagger + c_{-k}a_k$ which do not contribute to the resonant interaction in first order.[7]

In order to calculate the magnitude of the magnon-phonon coupling constant for $FeCl_2 \cdot 2H_2O$, we have measured $\Delta_x = 3600\ \text{cm}^{-1}$ (using infrared absorption). We have chosen $\lambda = -95\ \text{cm}^{-1}$ ($\lambda_0 = -104\ \text{cm}^{-1}$ for the free ion) and $\Delta_z = 715\ \text{cm}^{-1}$ so that the theoretical values for D and g are $9.56\ \text{cm}^{-1}$ and 2.26, consistent with the experimental values[9] of $9.58\ \text{cm}^{-1}$ and 2.23, respectively. The equivalent point charge Z' of the water molecule is given by $Z' = Z[(1 - d/2R)^{-4} - (1 + d/2R)^{-4}]$, where $Z = 2$ and the dipole spacing d is 0.23 ± 0.03 Å (obtained by comparing the parameters of free H_2O to those of H_2O in $FeCl_2 \cdot 2H_2O$[12]). We use $R = 2.43$ Å,[12] $\langle r^2\rangle = 0.392$ Å^2,[17] $S = 2$, $m =$ the mass of the water molecule, and $\omega_k(k=0) = 2\pi \times 31.5\ \text{cm}^{-1}$. Substituting these values into Eq. (4), we obtain a value for the magnon–optical-phonon coupling of $1.2 \pm 0.1\ \text{cm}^{-1}$, in remarkably good agreement with the *experimental value*[5] *of* $1.3 \pm 0.1\ \text{cm}^{-1}$.

The above values are for the ferromagnetic region. Since the phonon wave function is spread out over all sites, its amplitude on a particular *sublattice* in the AF region is only $1/\sqrt{2}$ times as large as for the ferromagnetic region; hence there is a reduction of $1/\sqrt{2}$ in the magnon-phonon coupling, as observed.[5,6] For the ferrimagnetic region, reduction factors of $\sqrt{\frac{2}{3}}$ and $\sqrt{\frac{1}{3}}$ give much better agreement with experiment (Fig. 1) than the factors used in Ref. 5. (There are complications, however, due to the fact that the spin-wave amplitudes are not enitrely localized to one sublattice, but these corrections are only ~ 10% for $FeCl_2 \cdot 2H_2O$.)

In conclusion, we note that point-charge crystal-field calculations are often poor. For example, attempts to calculate the magnon-phonon interaction in CoF_2 using a point-charge model[18,19] have resulted in values far smaller than the observed interaction. In $FeCl_2 \cdot 2H_2O$, however, covalency and charge-transfer effects are not so important in the binding (or motion) of the waters of hydration. For this reason we believe that in this case a point-charge calculation of the magnon-phonon interaction may be more accurate than would normally be expected. The excellent agreement thus obtained is, therefore, not completely fortuitous.

We wish to acknowledge helpful discussions with

K. W. H. Stevens and K. A. Hay. We also thank D. F. Nicoli and M. Tinkham for communicating their experimental results on $CoCl_2 \cdot 2D_2O$ prior to publication.

Note added in proof. It has just come to our attention that two neutron-diffraction groups have recently observed magnetic excitations interacting with high-*k* acoustic phonons. This interaction has been observed in $FeCO_3$ by Wrege, Spooner, and Gersch,[20] and in FeF_2 by Rainford and Houmann.[21] In addition, Lovesey[22] has made a calculation (based on a similar mechanism to the one described here) of the magnon–acoustic-phonon coupling in FeF_2 and finds good agreement with experiment.

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[2] G. Dolling and R. A. Cowley, Phys. Rev. Letters 16, 683 (1966); Phys. Rev. 167, 464 (1968).

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[11] We approximate the symmetry about the Fe^{2+} site as orthorhombic, with principal axes x, y, z. As an indication of the actual departure from orthorhombic symmetry, the Fe-Cl bond inclines 43.6° (instead of 45°) from the nearest-neighbor Fe-Fe bond and 12.3° from the axis of magnetization (z).

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[22] S. W. Lovesey, J. Phys. C (to be published).

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ERRATA

Mössbauer Studies on ^{57}Fe Atoms in Rare-Gas Matrices between 1.45 and 20.5 K, T. K. McNab, H. Micklitz, and P. H. Barrett [Phys. Rev. B 4, 3787 (1971)]. There is an error in the association between figure captions and the figures in Figs. 4, 5, and 6. The figure above Fig. 4 caption is Fig. 5, the figure above Fig. 5 caption is Fig. 6, and the figure above Fig. 6 caption is Fig. 4.

Calculation of the Spin-Lattice Coefficients of Gd^{3+} in CaF_2 Using a Point-Charge Model for the Crystalline Field, R. Calvo, M. C. G. Passeggi, and M. Tovar [Phys. Rev. B 4, 2876 (1971)]. We discovered an algebraic error in Eq. (12) where $B_{5g}^{(4)}$, $B_{5g}^{(6,a)}$, and $B_{5g}^{(6,b)}$ should have opposite signs. As a consequence, the value of $G_{5g}^{(2)}$ obtained from Eq. (11) is $G_{5g}^{(2)} = +0.07\ \mathrm{cm}^{-1}$ in disagreement in sign with the experimental value. There is also a typographical error in Eq. (9), where $B_{5g}^{(4)}$ should be multiplied by $(C_2^{(4)} - C_{-2}^{(4)})$.

Zener Theory, W. A. Smit and G. Vertogen [Phys. Rev. B 4, 2249 (1971)]. The denominator in the right-hand side of formula (24) should be replaced by $12[2 - f^2(R)]\,[4 - f^2(R)]$. This change is necessary because of a page make-up error and does not alter any of the results in the paper.