Simultaneous Excitation of a Magnon plus a Phonon in $CoBr_2 \cdot 2H_2O$: A New Type of Bound State?*

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The first observation of the excitation of a magnon plus a phonon is reported. The agreement between far-infrared measurements on $CoBr_2 \cdot 2H_2O$ and a simple theory is excellent. In addition, the transition probability is shown to be a consequence of a simple magnon-phonon interaction. We also discuss the possibility and evidence that this excitation corresponds to a *bound state* of a magnon plus a phonon.

$CoCl_2 \cdot 2H_2O$, $FeCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 2H_2O$, and $CoBr_2 \cdot 2H_2O$ have been widely studied because of their interesting magnetic,[1-6] microwave,[7] and far-infrared properties.[8-10] These compounds exhibit an extremely strong axial anisotropy, and at low temperatures order antiferromagnetically along the easy axis. As a consequence of this magnetic anisotropy, these materials do not exhibit the usual spin-flop transition, but are metamagnetic[1-6]: In the presence of a strong magnetic field (H_0) along the easy axis, there is a critical field H_{C1} above which the spins become ferrimagnetically ordered. At a still higher field H_{C2}, there is a second metamagnetic transition to the ferromagnetic state. These metamagnetic systems provide a convenient medium in which to examine low-lying excitations, since they can be studied in all three phases. For example, spin waves have been observed in each of these phases in $CoCl_2 \cdot 2H_2O$,[8] $FeCl_2 \cdot 2H_2O$,[9] and $CoBr_2 \cdot 2H_2O$[10] using far-infrared transmission measurements. In addition, multiple-magnon bound states have been observed in $CoCl_2 \cdot 2H_2O$[8] and $CoBr_2 \cdot 2H_2O$,[10] as well as transitions between these states in $CoCl_2 \cdot 2H_2O$.[7] Also in $FeCl_2 \cdot 2H_2O$[9,11] and $CoCl_2 \cdot 2H_2O$[8] the magnons were observed to interact with an optical phonon. In this Letter we discuss a new effect discovered in $CoBr_2 \cdot 2H_2O$: the simultaneous excitation of a magnon plus a phonon.

A typical far-infrared transmission spectrum for $CoBr_2 \cdot 2H_2O$ is shown in Fig. 1 for $H_0 = 45$ kOe and $T \sim 2$ K ($T_N = 9.5$ K). The experimental techniques used to obtain this spectrum are the same as those described in Refs. 8 and 10. The absorption lines shown in Fig. 1 are plotted along with those from other magnetic fields as the open circles in Fig. 2(a). The lower frequency (~15–25 cm^{-1}) absorption spectra are the spin waves ($k=0$ magnons), i.e., antiferromagnetic (a_1 and b_1), ferrimagnetic (c_1 and d_1), and ferromagnetic (e_1) resonance, in the respective metamagnetic phases. As described in Ref. 10, the straight lines through these data points correspond to a fit to a simple five-parameter spin-wave theory, similar to the one used in $CoCl_2 \cdot 2H_2O$[8] and $FeCl_2 \cdot 2H_2O$.[9] The two lines labeled e_2 and e_3 in Figs. 1 and 2(a) are the two- and three-magnon bound states, similar to those first observed in $CoCl_2 \cdot 2H_2O$.[8]

In this Letter we concentrate on the spectrum of excitations in the 33–43-cm^{-1} region, which are labeled A, B, C, D, and E in Fig. 2(a). These absorption lines have a g value of 6.19, which is *the same* as that of the spin waves. Therefore, these lines must correspond to some kind of single Co^{++} spin excitation. However, their energies are much higher than any of the magnons, which have only a small dispersion due to the large exchange anisotropy. Furthermore, these excitations cannot be low-lying crystal-field levels since these are expected[2]

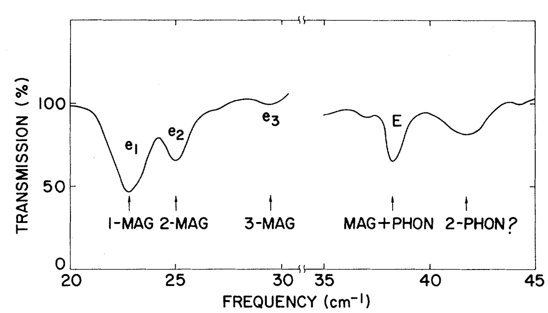

FIG. 1. Typical infrared transmission spectrum of $CoBr_2 \cdot 2H_2O$, taken at ~2 K and 45 kOe.

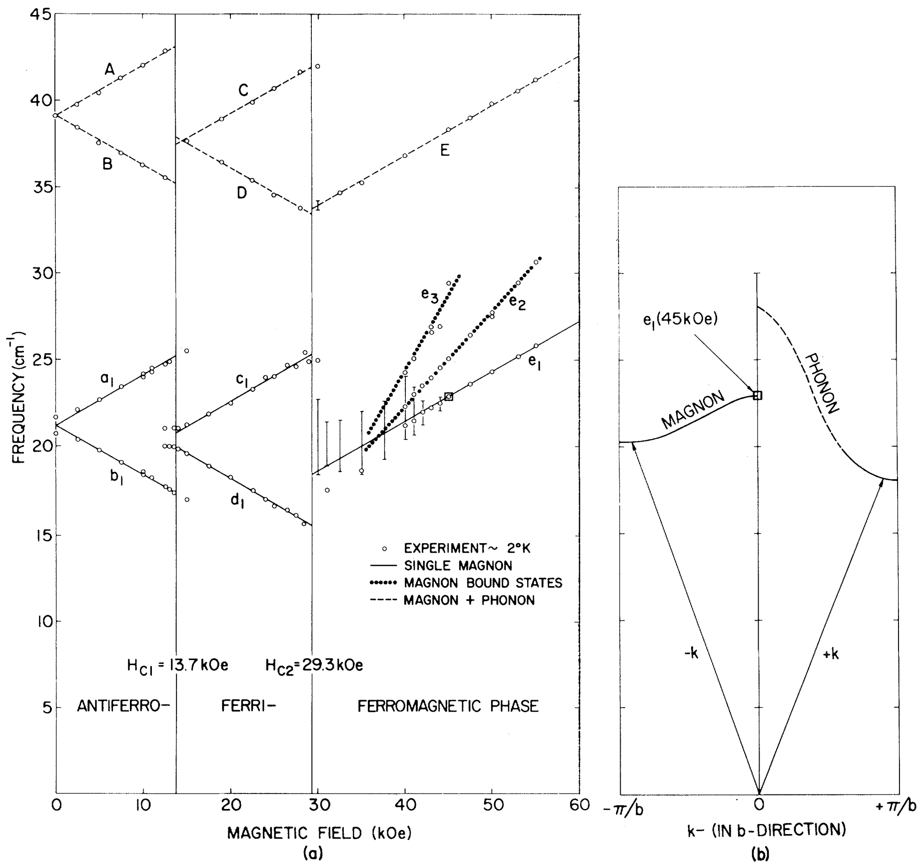

FIG. 2. (a) The magnetic-field dependence of the observed absorption frequencies; (b) the k depencence of the magnon and phonon at $H_0 = 45$ kOe.

at much higher energies (~150 cm^{-1}) and with very different g values (~1). The simplest remaining possibility is that the lines $A-E$ correspond to the excitation of a single magnon *plus* an additional, nonmagnetic excitation, presumably a phonon. In Fig. 2(b) we show the k dependence of the magnon and the nonmagnetic excitation (phonon) at $H_0 = 45$ kOe. (The magnon dispersion is calculated, while that of the phonon is schematic.) The single magnon excitation at $k=0$ [the box in Fig. 2(b)] is observed as the line labeled e_1 in Fig. 2(a) (the box at 23 cm^{-1} and 45 kOe). The higher-lying excitations ($A-E$) correspond to the simultaneous excitation of a phonon, which has in general a certain wave vector k, and a magnon at $-k$. To our knowledge, this is the first observation of such a magnon-plus-phonon excitation, although the excitation of a phonon plus two magnons has been observed in antiferromagnetic NiO.[12]

Since a_1-e_1 and $A-E$ both involve magnons, we should be able to compare their field-dependent energies. Note that C and D intersect just above H_{C1} [Fig. 2(a)], while c_1 and d_1 do not intersect. Similarly D and E almost intersect at H_{C2}, while d_1 is ~3 cm^{-1} lower than e_1 at H_{C2}. These differences are indicative of the fact that a_1-e_1 are magnons excited at $k=0$, while $A-E$ are in general associated with some other region of k space. In fact, one can use the relative energies of $A-E$ to determine where in k space they are excited. The theoretical fit[10] in Fig. 2(a) (dashed lines) is for magnons excited at the Brillouin-zone boundary in the b direction. The excellent agreement with experiment is evidence that the magnons are associated with k near π/b. This agreement is obtained using only the *same* five parameters from the $k=0$ spin-wave fit plus the energy of the nonmagnetic excitation (phonon). This energy was found to be 18.0 cm^{-1}.

We believe that this nonmagnetic excitation is an optical phonon for the following reasons: (i) A phonon is the most common nonmagnetic excitation; (ii) both $CoCl_2 \cdot 2H_2O$[8] and $FeCl_2 \cdot 2H_2O$[9,11] have optical phonons with quite low frequencies [$\nu(k=0) \sim 30$ cm^{-1}], so that it is not unreasonable to find one as low as 18.0 cm^{-1} in $CoBr_2 \cdot 2H_2O$; and (iii) an interaction between a magnon and a *phonon* can account for the transition probability, as we now show. We consider a simple magnon-phonon coupling of the form $\mathcal{H}' = A\sum_i u_i S_i^x S_i^z$, where u_i is the phonon displacement at site i and A the magnon-phonon coupling constant. Second-quantizing this interaction, we obtain

$$\mathcal{H}' = \sum_k A_k (c_k^\dagger + c_{-k})(a_{-k}^\dagger + a_k) = \sum_k A_k ([c_k^\dagger a_k + c_{-k} a_{-k}^\dagger] + [c_{-k} a_k + c_k^\dagger a_{-k}^\dagger]), \quad (1)$$

where $c_k^\dagger$ (c_k) and $a_k^\dagger$ (a_k) are the creation (annihilation) operators for the phonons and magnons, respectively. The first bracketed term is the familiar magnetoelastic interaction,[13] which admixes an excited magnon with a phonon and vice versa, as observed in $FeCl_2 \cdot 2H_2O$[9,11] and $CoCl_2 \cdot 2H_2O$[8], as well as in other materials.

The second bracketed term of Eq. (1), however, is much less well studied.[14] Treated as a perturbation, this term couples the ground state, $|0\rangle$, with the state $|k, -k\rangle$ which contains a phonon with wave vector k and a magnon with $-k$. Using perturbation theory to second order, we may schematically write down the new, admixed wave functions as[15]

$$|0\rangle' \sim \frac{|0\rangle - \sum_k \alpha_k |k, -k\rangle}{(1 + \sum_k \alpha_k^2)^{1/2}},$$
$$|k, -k\rangle' \sim \frac{|k, -k\rangle + \alpha_k |0\rangle}{(1 + \sum_k \alpha_k^2)^{1/2}}. \quad (2)$$

Here $\alpha_k \sim A_k / [E_P(k) + E_M(-k)]$, where E_P and E_M are the phonon and magnon energies, respectively. Physically, the magnon-phonon interaction couples the zero-point motion of the magnons and phonons. There are several important consequences of the admixture shown in Eq. (2). In particular, there is now a nonzero matrix element of the magnetic dipole operator, $g\mu_B S_z h_z$, between the admixed states $|0\rangle'$ and $|k, -k\rangle'$ which is proportional to α_k. Thus, the finite transition probability of exciting a magnon plus a phonon is accounted for by a simple magnon-phonon interaction. From Eq. (2) it is evident that both magnons and phonons are admixed into the ground state by the interaction. The magnon admixture gives rise to a decrease in the saturation magnetization, as observed in several of these compounds.[1-3,16] The admixture of phonons into the ground state may be partially responsible for the changes in the easy-axis lattice constant observed upon cooling through T_N[17] as well as upon sweeping the external field through H_{C1} and H_{C2}.[6]

Finally we discuss the possibility that this excitation is actually a *bound state* of a magnon and a phonon, with a certain binding energy. That is, perhaps this absorption does *not* correspond to exciting a phonon with a given k and an *independent* magnon with $-k$. Generally speaking, there certainly are magnon-phonon interactions [not included in Eq. (1)] which would tend to lower the energy of a magnon and a phonon excited in close proximity relative to the continuum of magnon plus phonon states. In addition, the formation of such a bound state is made easier by the narrow widths of the magnon and phonon bands expected in $CoBr_2 \cdot 2H_2O$. In this case, the observed $k \sim \pi/b$ character of the excitation would be accounted for as follows: Assuming that the phonon involved corresponds to the same motion of the water molecules as found in $FeCl_2 \cdot 2H_2O$,[11] the lowest phonon energy occurs at $k \sim \pi/b$. The bottom of the continuum would then be made up of a relatively large density of $k \sim \pi/b$ phonon and magnon states, from which the appropriate magnon-phonon interaction could split off a bound state, which would also have this $k \sim \pi/b$ character.

Experimentally, the observed linewidth of this magnon-plus-phonon excitation (Fig. 1) is much narrower than what we would expect for the width of the continuum, thus supporting its identification as a bound state. This assignment could be checked if we had an independent measure of the phonon energy. This we could compare to the apparent energy of 18.0 cm^{-1}, to see if there was any binding. There is a *possibility* of such a measure: Between 40 and 43 cm^{-1} we observe a somewhat broad, field-independent absorption (Fig. 1). If we assume (i) that this absorption is a two-phonon excitation, *and* (ii) that it is dominated by the same phonons as those associated with the magnon-plus-phonon excitation, we obtain for the noninteracting phonon energy $\frac{1}{2}(40-43) = 20-21.5$ cm^{-1}. Comparing this energy to 18.0 cm^{-1}, we believe that we have observed the excitation of a *bound state* of a magnon and a phonon, which has a binding energy as large as 2.0 cm^{-1}. Perhaps future Raman or inelastic neutron scattering experiments could confirm this identification.

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Note added.—The probability that this excitation is indeed a bound state of a magnon and a phonon is supported by recent theoretical calculations of Ngai, Ruvalds, and Economou which are described in the following Letter.[18]

*The experimental work reported here was performed while the authors were at the Division of Engineering and Applied Physics, Harvard University, Cambridge, Mass. 02138.

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Bound Magnon-Phonon Pairs in Metamagnetic Systems*

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We calculate the magnon-phonon coupling for metamagnetic systems of the type FeCl $\cdot 2H_2O$. The coupling, which is derived from a microscopic point of view, is strong enough to bind a magnon to a phonon in some metamagnetic materials. An analysis of the coupling is presented for different systems, and the results are related to recent experimental data of Torrance and Hay.

Recently considerable efforts have been made to understand the elementary excitations, i.e., magnons and phonons, in metamagnetic systems such as $CoCl_2 \cdot 2H_2O$, $FeCl_2 \cdot 2H_2O$, and $CoBr_2 \cdot 2H_2O$. The excitations determine the far-infrared properties of these materials. The inter-