Light Scattering from Phonons and Magnons in $CoCl_2 \cdot 2H_2O$

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A light scattering study of cobalt chloride dihydrate is reported. Emphasis is placed upon phonon–magnon interactions in the antiferromagnetic phase. Data taken at $T = 1.6$ K and magnetic fields from 0 to 5 T confirm the conclusion of Schneider and Weitzel that the ferrimagnetic–antiferromagnetic phase transition is first-order and that a large hysteresis is observable at temperatures below 4.2 K.

INTRODUCTION

The dihydrates of the iron-group halides of MX_2, where M = Mn, Fe, Co, Ni and X = Cl, Br, are all structurally similar to $CuCl_2 \cdot 2H_2O$.[1] It is known that at room temperature the chlorides of Mn, Fe and Co and the bromides of Mn and Co are in fact isomorphous.[1–4] The space group for these compounds at room temperature is $C2/m$.[2–5] We shall abreviate $CoCl_2 \cdot 2H_2O$ as CC2 in what follows, with similar notations for its isomorphs (e.g. FC2 for $FeCl_2 \cdot 2H_2O$ and NB2 for $NiBr_2 \cdot 2H_2O$).

CC2, CB2, FC2 and NC2 are linear chain systems that are known to exhibit metamagnetic behavior.[6–11] The other structurally similar compounds may also be metamagnetic, e.g. NB2. Metamagnetic materials are those which are highly anisotropic and whose magnetic field induced phase transitions at low temperatures are characterized by simple spin reversals. This is in contrast with spin-flop materials such as MnF_2 which are fairly isotropic and whose transitions are characterized by spin rotations.[12] Metamagnetism is discussed at length and several examples of metamagnetic compounds (including CC2, CB2, FC2 and NC2) are given in the recent review article by Stryjewski and Giordano.[12] The behavior of CC2 in its different metamagnetic phases and its behavior at the phase transitions themselves have been the focus of much research interest.

Interest in CC2 was generated with the report of an anomaly in the heat capacity at 17.2 K by Shinoda *et al.*[13,14] This anomaly was taken to indicate a transition from a paramagnetic (P) to an antiferromagnetic (AF) state. Magnetization and susceptibility studies were also performed on CC2 about the same time by Kobayashi and Haseda[8] and independently by Narath.[9,15] The *b*-axis magnetic susceptibility showed a sharp anomaly at 17.5 K, while the *b*-axis magnetization measured at 4 K was seen to possess two sharp discontinuities. This prompted the proposal that CC2 undergoes two phase transitions as a function of magnetic field at low temperatures. The first transition was from the AF state where all the spins of a sublattice are along *b* to an intermediate state, while the second was from the intermediate to the P state. Kobayashi and Haseda[8] thought the intermediate phase to involve spin flopping. Oguchi and Takano[16] pointed out that this was not possible and instead proposed that the intermediate phase could be explained as a 4-sublattice spin ordering arrangement with all the spins remaining along *b*, the easy magnetization direction. Narath[17] noted that such an arrangement was not consistent with the observed magnetization in the intermediate phase region but that a 6-sublattice spin ordering arrangement was.

Morosin and Graeber,[2] using X-ray techniques, determined CC2 to be a monoclinic compound whose space group is $C2/m$ at room temperature. They also credit Vainshtein[18] with obtaining the first direct evidence of its structure via electron diffraction. Later, Morosin[1] confirmed that the crystallographic structure remains the same down to 5 K. Cox *et al.*[19,20] showed directly using neutron diffraction that the magnetic ordering at 4.2 K and zero field is antiferromagnetic and the ordering in the ferrimagnetic (intermediate) phase was indeed that proposed by Oguchi and Takano[16] and modified by Narath.[17]

Magnon bound states or spin clusters were observed by Date and Motokawa[21–23] and have been investigated in great detail experimentally via far-IR transmission studies and also theoretically by Torrance and Tinkham[24–26] and by Nicoli and Tinkham.[27] These far-IR measurements provided the first direct observation of the magnon bound states in CC2.

Kjems *et al.*[28] have used inelastic neutron scattering to determine the dispersion of the two one-magnon branches at zero field in the deuterated form of CC2. Using a simple model to analyze their data, the transverse anisotropy was found to decrease rapidly from its value at small wave vectors. This indicated to them that the responsible mechanism for the anisotropy has a long range and possibly is not superexchange. They were unable to resolve the associated phonon and did not include its effect in their model.

The IR spectrum of the water molecules' internal vibrations has been of interest to several workers. Fifer and Schiffer[29] were interested in determining the force constants from the observed frequencies. Ichida *et al.*[30] were able to assign unambiguously the observed frequencies as rocking and wagging modes of the water molecule. In a series of papers, Srivastava *et al.*[31–33] examined the intensities and half-widths and calculated mechanical and electrical anharmonicities from them.

There has also been great interest recently in the magnon–phonon interaction observed in CC2, CB2 and FC2. Besides the work performed on CC2, Hay and

CCC-0377-0486/79/0008-0335$02.50

Torrance[34,35] also observed magnon–phonon interaction in far-IR measurements on FC2 and CB2. In addition, Raman scattering has been used to study the magnon–phonon interaction in FC2 as a function of temperature and field by Kinne *et al.*[36] Later, Graf and Schaack[37] were able to obtain a more detailed temperature dependence of the coupling in FC2 using Raman spectroscopy. Early work in obtaining microscopic expressions for the magnon–phonon coupling was done by Torrance and Slonczewski[38] and by Ngai *et al.*[39] Economou *et al.*[40] succeeded in obtaining a detailed microscopic magnon–phonon Hamiltonian for CC2, CB2 and FC2. The interaction was attributed to a modulation of the crystal field at the magnetic ion site by the vibration of the waters of hydration.

EXPERIMENTAL

Most of the data here were obtained using the 4579 Å line of a Coherent Radiation Model 52HD argon laser. The power output of this line was rated at 50 mW and had a long-term stability of about 3% after a 30 min warm-up period. A Spectra-Physics Model 310-21 polarization rotator was used to change the incident polarization.

The Nb_3Sn magnet used here was a 28 cm long solenoid with a 20 cm outside diameter and a 3.2 cm bore diameter. It was equipped with three midplane ports allowing transverse optical access as well as a magnetic resistance probe for field value determination. Although the highest field value attained in this work was only about 55 kOe, fields of 140 kOe also may be achieved routinely.

The spectrometer used was a Spex Model 1401 0.85 m Czerny–Turner double spectrometer with the two gratings ruled at 1200 grooves mm^{-1} and blazed at 500 mm. The instrument was also equipped with a stepper/synchronous motor and wavenumber drive. The light output of the spectrometer was detected by an ITT FW-130 photomultiplier and had a quantum efficiency of about 15% at 4579 Å. The operating voltage was supplied by a Keithley Model 244-2441 high-voltage power supply. Dark count rates of less than 3 counts s^{-1} were obtained by cooling the photomultiplier to about −30 °C using a Products for Research Model TI-104TS-RF thermoelectric cryostat. Photoelectron pulses were then counted electronically using a Spex Model PC-1 photon counting system and the output analog signal displayed on a Yokagawa Electric Works strip-chart recorder.

It is known that $CoCl_2$ and water will form three stable compounds as a function of temperature: $CoCl_2$, $CoCl_2 \cdot 2H_2O$ and $CoCl_2 \cdot 6H_2O$. At room temperature the hexahydrate is the stable compound while above 52.2 °C, CC2 is the stable hydration state. At still higher temperatures the stable compound is, of course, anhydrous $CoCl_2$.

At room temperature CC2 may interact with the environment. It may extract water vapor from the air to form the hexahydrate, or in a dry atmosphere or vacuum it may actually give off water forming an opaque, pinkish layer of $CoCl_2$ on the crystal surface. These problems are alleviated somewhat by coating the surface of the samples with an inert oil, e.g. mineral oil, or immersing them in toluene, but care in handling CC2 is still very necessary.

CC2 may be grown from a saturated aqueous solution by slow evaporation at a temperature above 52.2 °C (e.g. 70 °C). CC2 crystals have a pronounced preferred growth habit along {001} (the *c*-axis) and exhibit well-developed (110) type faces.[12] These features enable a crystal to be oriented solely from the external morphology. The angles between the (110) type faces are approximately 80° and 100°; so, following Torrance, aluminum blocks having V-grooves of these angles were constructed. A crystal fitting into the 100° groove would have a^* ($a^* = a \cos\beta$) pointing out of the groove, c along the groove axis, and b perpendicular to a^* and c.

The weak hydrogen bonding between chains allowed crystals to be easily cleaved in the b–c plane using a sharp razor blade when held in a V-block. Cleaving the crystal perpendicular to the c-axis is more difficult and several different methods were tried during the course of this work. The method that gave the best results with the fewest complications was to make the cut using a diamond saw while applying stress (perpendicular to the c-axis) to either side of the proposed cut via the V-blocks, i.e. the crystal is mounted in two V-blocks, one either side of the proposed cut. The applied stress seemed to have the effect of forcing the chains to remain together when the hydrogen bonds would otherwise have been broken, and use of a diamond saw minimized any lateral fraying along the c-axis. Adequate optical surfaces were then obtained by polishing using a suitable abrasive, i.e. Linde A (0.1 μm alumina) in mineral oil. The final typical sample had a length of about 5 mm with a triangular a–b cross-section of about 8 mm^2.

The data reported here were taken using 4579 Å radiation and 50 mW laser power. Representative traces are given in Figs. 1 and 2. In all of the data, the spectrometer slits were set at 30/100/30 μm with a resulting instrumental resolution of 0.7 cm^{-1}. A scan speed of 5 cm^{-1} min^{-1} with a 5 s RC time constant, a chart speed of 5 cm min^{-1} and 100 counts s^{-1} full-scale deflection were used. The temperature ranged from 1.6 to 1.8 K, and the geometry was $y(z^y_z)x$.

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate two strong scattering features near 30 cm^{-1}. The frequencies and intensities of these features change with applied magnetic field in a manner characteristic of coupled oscillators. At low fields in Fig. 1 the intense feature at lower energy (about 29 cm^{-1}) is assigned as a B_g symmetry phonon, on the basis of its observed scattering polarizability. The weaker feature at about 31 cm^{-1} is assigned as the lower energy component of the antiferromagnetic magnon, which is split in zero magnetic field by the large transverse anisotropy in $CoCl_2 \cdot 2H_2O$. These coupled modes have been studied extensively in earlier IR work, and a complete plot of their energies is given in Fig. 3, following Nicoli and Tinkham.[27] In zero field phonon–magnon coupling with the higher energy magnon branch (at 35 cm^{-1} and labeled a_1 in Fig. 3) is forbidden by symmetry for $FeCl_2 \cdot 2H_2O$ but permitted in $CoCl_2 \cdot 2H_2O$. This

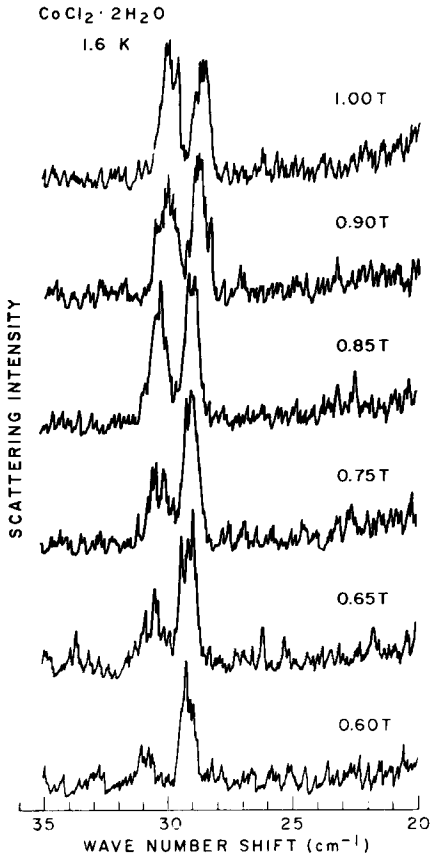

Figure 1. Raman spectra of coupled magnon and phonon states in $CoCl_2 \cdot 2H_2O$, at fields from 0.6 to 1.0 T.

symmetry argument is proved group theoretically by Cracknell[41] and was suggested earlier to the present authors by Torrance[42] and by Graf.[43]

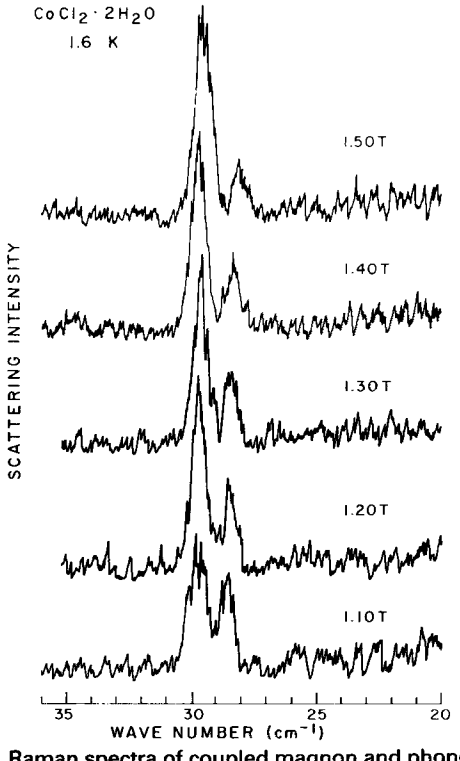

Figure 2. Raman spectra of coupled magnon and phonon states in $CoCl_2 \cdot 2H_2O$, at fields from 1.1 to 1.5 T.

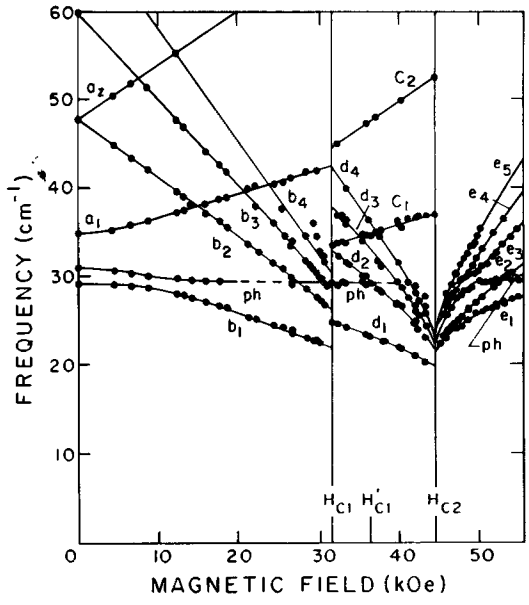

Figure 3. Energy levels vs. magnetic field for $CoCl_2 \cdot 2H_2O$ (from Ref. 24).

An accurate value of the phonon–magnon interaction energy may be obtained from the distance of closest approach of the two well-resolved scattering features illustrated in Figs. 1 and 2; the interaction energy is exactly half the energy spacing at closest approach, and we evaluate it as 0.60 ± 0.05 cm^{-1}, in good agreement with the value 0.55 ± 0.05 cm^{-1} obtained by Torrance and Tinkham.[24–26]

At fields greater than 1.5 T we observe substantial disagreement between our measured magnon energies and the experimental data of Torrance and Tinkham.[24] This is illustrated in Fig. 4, where our data are compared with the smooth curves which were fitted to the results (see Fig. 3) of Torrance and Tinkham.

All of our data were obtained after the samples had been cycled at 1.6 K to magnetic fields exceeding 10 T. The measured energies for the magnon branch under these conditions were not consistently reproducible, as shown in Fig. 5, where data differ slightly from those in Fig. 4. In each case, however, the magnon data fail to follow the predicted curve b_1 but instead extrapolate to the d_1 curve of the one-magnon excitation in the ferrimagnetic phase.[1] Since our sample orientation was done in a simple way, using the external morphology, we do not believe that this difference can be attributed to misorientation and consequent change of magnon

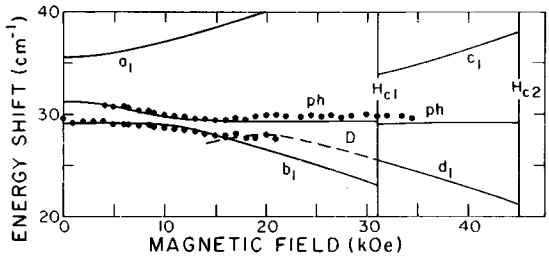

Figure 4. Energy levels vs. magnetic field for coupled phonon–magnon system in $CoCl_2 \cdot 2H_2O$ (present work). b_1 and d_1 are the calculated one-magnon levels in the antiferromagnetic and ferrimagnetic phases, respectively.

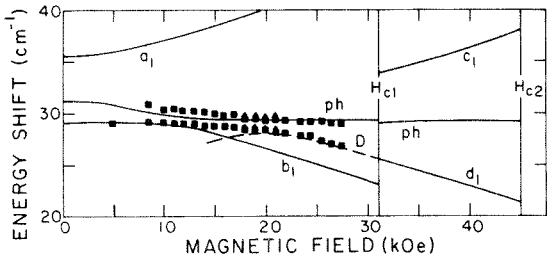

Figure 5. Phonon–magnon energies from Raman scattering in $CoCl_2 \cdot 2H_2O$. Two data sets are plotted here; they are slightly different from the results shown in Fig. 4.

g-value; instead we believe that it is due to an unexpectedly large hysteresis encouraged in lowering the samples from the ferrimagnetic phase into the antiferromagnetic phase. That is, we believe that our sample was predominantly ferrimagnetic above $H = 1.9 \pm 0.2$ T, where the cross-over behavior illustrated in Figs. 4 and 5 was manifest. This interpretation is compatible with the data and analysis of Schneider and Weitzel,[44] graphed in Fig. 6. Their results show that the antiferromagnetic–ferrimagnetic phase boundary is first-order at all H and T (solid circles), whereas the paramagnetic (or ferromagnetic) to antiferromagnetic transition is second-order (open circles). Above $T = 5$ K they observe no measurable hysteresis, but at 2.1 K they observe a 0.5 T hysteresis, with the AF/FI boundary encountered at about 3.2 T with increasing field and about 2.7 T with decreasing field. Our results at a lower temperature of 1.6 K given an even greater hysteresis region of 1.3 ± 0.2 T; our result is plotted as the × on Fig. 6. Nicoli also reports ferrimagnetic magnon features persisting into the antiferromagnetic phase and discusses the coexistence of FI and AF domains. For further details of the hysteresis behavior in $CoCl_2 \cdot 2H_2O$ see Kuramitsu[45] and Ono.[46]

We attempted in our light scattering experiments to observe phonon–magnon coupling in the ferrimagnetic

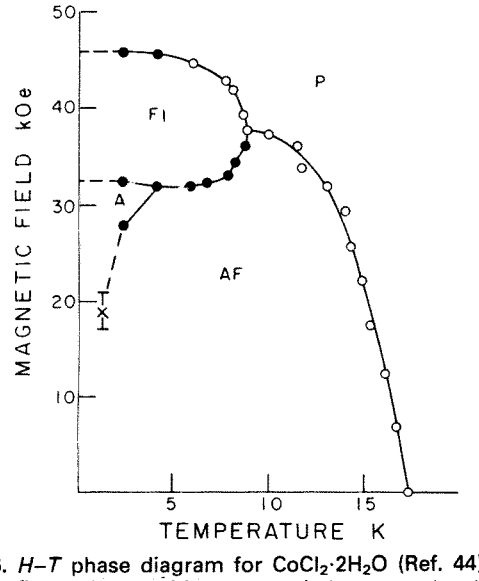

Figure 6. H–T phase diagram for $CoCl_2 \cdot 2H_2O$ (Ref. 44). Solid circles are first-order transitions; open circles, second-order. P, FI and AF designate paramagnetic, ferrimagnetic and antiferromagnetic. The paramagnetic phase is equivalently referred to as ferromagnetic in the text; since no ferromagnetic phase exists at $H = 0$, the distinction between ferromagnetic and paramagnetic is semantic.

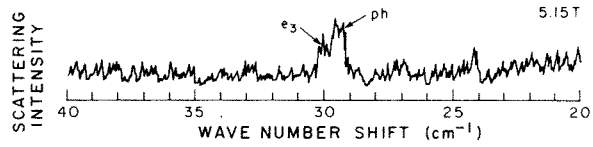

Figure 7. Scattering from phonons and three-magnon bound states in $CoCl_2 \cdot 2H_2O$.

and ferromagnetic phases as well as the antiferromagnetic phase. These attempts were very marginally successful. Figure 7 illustrates one spectrum obtained in the ferromagnetic phase. At $H = 5.15$ T the phonon feature at about 29.5 cm^{-1} displays a barely resolvable shoulder at 30 cm^{-1}. Examination of the IR data in Fig. 3 shows that the three-magnon bound state interacts with the B_g phonon for fields near 5 T, such that a doublet might be expected in the Raman spectra near this value of magnetic field, with the weaker feature lying at energies just above 30 cm^{-1}. With this motivation, we have labeled the two observed features according to Torrance's notation 'ph' for phonon and 'e_3' for the three-magnon bound state. Poor signal-to-noise ratios prevented further investigation of the ferromagnetic phase.

Finally, an attempt was made to observe multiple-magnon bound states in the antiferromagnetic phase. It was expected that the intrinsic cross-sections of these features would be too weak for detection, but that interaction with the B_g phonon would provide sufficient intensity in some cases. Figure 8 illustrates some representative data. At $H = 1.9$ T three weak features are observed at 41.2, 36.7 and 35 cm^{-1} (labeled A, B, C respectively). These features become extremely indistinct in the trace at $H = 2.0$ T, also shown in Fig. 8. We could not obtain sufficiently good signal-to-noise to follow these features as a function of field and thereby identify them. However, feature A at 41 cm^{-1} does agree well with the energy of the b_3 three-magnon bound state at $H = 1.9$ T in Fig. 3, and the odd-numbered bound states may interact strongly with the phonon. Moreover, the energy of the upper branch of the one-magnon excitation (a_1 in Fig. 3) is approximately 38 cm^{-1} at $H = 1.9$ T and therefore agrees reasonably well with feature B. Feature C at 35 cm^{-1} agrees with the energy of the two-magnon bound state b_2; however, strong coupling of b_2 to the phonon is not

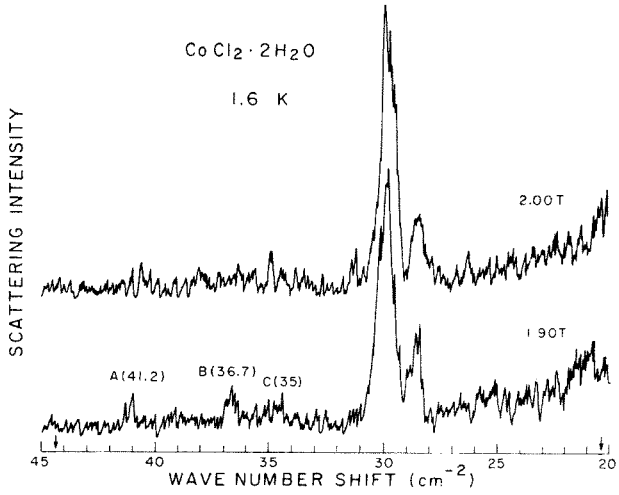

Figure 8. Weak scattering features in $CoCl_2 \cdot 2H_2O$ at $T = 1.6$ K and $H = 2$ T.

expected, and so this assignment is more speculative. A broad weak feature near 21 cm^{-1} is also observed in Fig. 8. This broad line was observed with both 647 and 458 nm excitation; it is not assigned, but may be a lower energy B_g phonon hypothesized by Economou *et al.*[40]

SUMMARY AND CONCLUSIONS

Raman scattering has been observed from a coupled phonon–magnon system in $CoCl_2 \cdot 2H_2O$. The effective gyromagnetic ratio at low fields is approximately 6.5 for g_z, and the phonon–magnon coupling constant is 0.60 ± 0.05 cm^{-1}; both are in accord with earlier IR measurements. The value of H_{C1}, the critical field at the ferrimagnetic–antiferromagnetic phase boundary, exhibits large hysteresis, and is found to lie at 1.9 ± 0.2 T for decreasing fields; this hysteresis is in accord with the work of Schneider and Weitzel at slightly higher temperatures. Weak scattering is observed and attributed to multiple-magnon bound states in both ferromagnetic and antiferromagnetic phases.

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Received 29 June 1979