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# Raman Light Scattering from Excitons and Magnons in Cobalt Fluoride

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We have observed one-particle, inelastic, polarized light scattering from low-lying excitons and magnons in single-crystal cobalt fluoride ($CoF_2$) at 2°K. Because of the orbital nature of these excitations, the cross sections ($10^{-33}$–$10^{-32}$ $cm^2/sr$) are much larger than for one-magnon scattering in the other case, which has been measured ($FeF_2$, ~$10^{-35}$ $cm^2/sr$). Our measured cross sections are in good agreement with a recent calculation by Ishikawa and Moriya.

The first observation[1] of one-magnon light scattering in magnetic insulators was in $FeF_2$ where the magnons are predominantly spinlike excitations and the scattering mechanism requires spin-orbit coupling in the virtual intermediate state in order to be finite for an electric dipole process.[2] Subsequent measurements have concentrated on two-magnon scattering.[1,3] This is because for spinlike excitations it is a stronger process (proceeding via inter-ion exchange coupling[1,4]), and in low-anistropy materials such as manganese and nickel compounds, the one-magnon energy is only a few $cm^{-1}$, and hence difficult to measure. We wish to report here the observation of scattering by single magnons and low-lying excitons in $CoF_2$. The latter arise from excitations within the low-lying $^4T_1$ levels of the cobalt ions, split by spin-orbit coupling, orthorhombic crystal field, and inter-ion exchange interactions. The scattering mechanism involves a direct coupling of the $\vec{E}$ vector of the incident light to the orbital part of the excitations, and this gives rise to larger cross sections than for spin excitations. In fact, the exciton scattering is comparable in magnitude with the phonon scattering. Measured cross sections are in good agreement with those recently calculated by Ishikawa and Moriya.[5]

The symmetry group of $CoF_2$ below $T_N$ is $D_{4h}{}^{14}(D_{2h}{}^{12})$ and branches of the excitation spectrum at $\vec{k}=0$ are labeled by unitary subgroup representations $\Gamma_1{}^+$, $\Gamma_2{}^+$, and $\Gamma_3{}^+ + \Gamma_4{}^+$. In the absence of off-diagonal inter-ion exchange coupling, all branches show the sublattice degeneracy of 2. Without this restriction the $\Gamma_1{}^+$, $\Gamma_2{}^+$ pair may show a Davydov splitting while $\Gamma_3{}^+$ and $\Gamma_4{}^+$ are required to be degenerate by the antiunitary operators of $D_{4h}{}^{14}(D_{2h}{}^{12})$. The low-lying electronic levels of the $Co^{2+}$ ion have been studied by Johnson, Dietz, and Guggenheim[6] and Gladney.[7] The dispersion of the low-lying excitations in $CoF_2$ has been measured by neutron scattering,[8] and the ones we will be concerned with here are the magnons with an energy of 37 $cm^{-1}$ at $\vec{k}=0$, the Davydov-split $\Gamma_1{}^+$, $\Gamma_2{}^+$ excitons at 169 $cm^{-1}$ and 204 $cm^{-1}$, and the $\Gamma_3{}^+ + \Gamma_4{}^+$ branch at 194 $cm^{-1}$. In addition there are four ($\Gamma_1{}^+$, $\Gamma_2{}^+$), and four ($\Gamma_3{}^+ + \Gamma_4{}^+$) branches around 800 $cm^{-1}$ which have not yet been observed by any technique. Light scattering is allowed by symmetry from all branches, but only $\Gamma_2^+$, $\Gamma_3^+$, and $\Gamma_4^+$ are magnetic-dipole infrared active. The nonvanishing elements of the scattering tensor for the corepresentations can be determined group-theoretically and are given by[9]

$$D\Gamma_1^+ = \begin{pmatrix} a & 0 & 0 \\ 0 & a^* & 0 \\ 0 & 0 & c \end{pmatrix}, \quad D\Gamma_2^+ = \begin{pmatrix} 0 & d & 0 \\ d^* & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix},$$

$$D\Gamma_3^+, \Gamma_4^+ = \begin{pmatrix} 0 & 0 & f \\ 0 & 0 & 0 \\ g & 0 & 0 \end{pmatrix}, \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -f^* \\ 0 & -g^* & 0 \end{pmatrix}. \qquad (1)$$

The individual modes can be observed by a proper choice of scattering geometry. Note that the scattering tensor is not antisymmetric, as is the case for spin-like magnons, where $f=-g$ and $\mathrm{Im}(f)=\mathrm{Im}(g)$, nor symmetric as is the case for phonons, and we have observed this in the relative scattering cross sections. As Fleury and Loudon[10] have pointed out, this lack of antisymmetry is expected for $CoF_2$ because of the orbital nature of the low-lying excitations, and is not observed in $FeF_2$.

A single crystal of $CoF_2$, oriented with faces normal to the [100], [010], and [001] directions, was immersed in liquid helium at 2°K. The beam from a 60-mW He-Ne laser was incident vertically and the 90° scattered light analyzed with a 1-m double monochromator and detected by conventional photon-counting techniques. The results obtained are shown in Figs. 1 and 2 and summarized in Table I. Scattering from the $\Gamma_2^+$ exciton at 204 $cm^{-1}$ was below the sensitivity limit of our system. The assignment of the electronic scattering is made on the basis of its polarization properties, energy, and qualitative temperature dependence. All of the lines broaden rapidly towards $T_N$ (e.g., the $\Gamma_1^+$ width goes from 2 to ~40 $cm^{-1}$) and the scattering cross section essentially goes to zero at this temperature. Our polarization measurements of the 169-$cm^{-1}$ line show that this mode is the $\Gamma_1^+$ and positively determines the sign of the Davydov splitting, i.e., $\Gamma_1^+$ is lower than $\Gamma_2^+$. The absorption coefficient of $CoF_2$ at 6328 Å is 1 $cm^{-1}$ for $E \parallel c$ and 7 $cm^{-1}$ for $E \perp c$.[11] Thus the effective scattering volume is different for these two directions of excitation. The laser beam was kept close to the surface of the crystal to minimize reabsorption of the scattered light. Relative cross sections were determined by comparison with the $E_g$ phonon at 256 $cm^{-1}$ which has a symmetric scattering tensor. An approximate absolute cross section was obtained by measuring the 992-$cm^{-1}$ line of benzene and using Skinner and Nilsen's[12] value for its absolute cross section. In table I we also show results for the strongest phonon scattering, viz., that from the $A_{1g}(\Gamma_1^+)$ and $E_g(\Gamma_3^+ + \Gamma_4^+)$ modes.[13] Macfarlane and Ushioda[14] have already reported room-temperature measurements of all of the $\vec{k}=0$ phonons. Both the $A_{1g}(\Gamma_1^+)$ and $E_g(\Gamma_3^+ + \Gamma_4^+)$ modes couple appreciably to electronic excitations at low temperature. This was first shown for $E_g(\Gamma_3^+ + \Gamma_4^+)$ by Allen

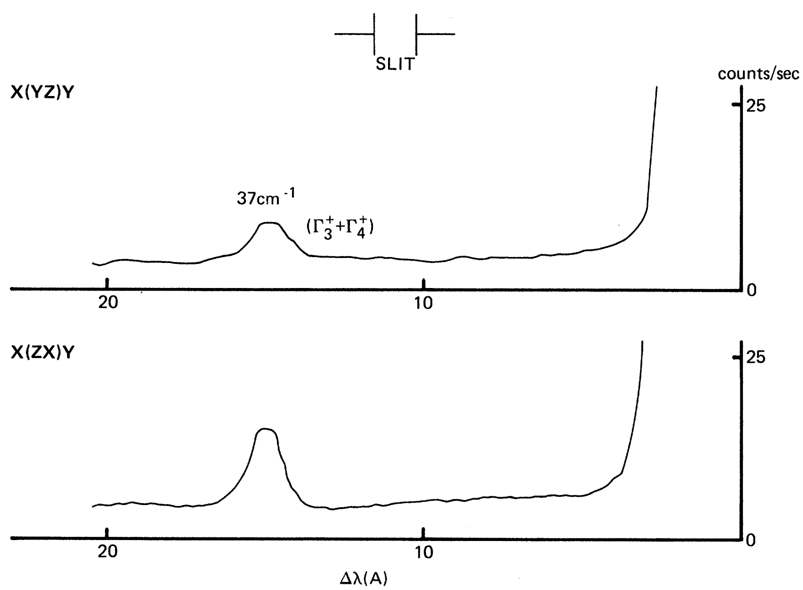


FIG. 1. Polarized spectra of one-magnon light scattering in $CoF_2$ at 2°K. The scale is linear in the wavelength shift from the He-Ne laser line at 6328 Å.

and Guggenheim[15] who measured a temperature-dependent absorption cross section (which, in contrast to light scattering, is zero for the pure phonon mode), and a linewidth minimum around $T_N$. We have confirmed these linewidth measurements and also find a very similar behavior for the $A_{1g}(\Gamma_1^+)$ mode. Further details will be presented in the near future.

The differential extinction coefficient for incident and scattered polarizations $\mu$ and $\nu$ (defined as the fraction of light scattered per centimeter of path per steradian) can be written[16]

$$\left(\frac{dh}{d\Omega}\right)_{\mu\nu} = \int_0^\infty d\omega \, \frac{\omega_0\omega^3}{2\pi c^4} \int_{-\infty}^{\infty} dt\, e^{i(\omega-\omega_0)t} \langle \alpha_{\mu\nu}(0)\alpha_{\nu\mu}(t)\rangle, \tag{2}$$

where $\omega_0$ is the incident frequency and $\omega$ the scattered frequency. To obtain the cross section we must divide by $2.8\times10^{22}$, the number of cobalt ions per cubic centimeter. The matrix elements of the polarizability operator for the Stokes scattering from excitation $|n\rangle$ are

$$\langle 0|\alpha_{\mu\nu}|n\rangle = \sum_u \left[\frac{\langle 0|P_\mu|u\rangle\langle u|P_\nu|n\rangle}{E_u-E_0-h\omega} + \frac{\langle 0|P_\nu|u\rangle\langle u|P_\mu|n\rangle}{E_u-E_0+h\omega}\right]. \tag{3}$$

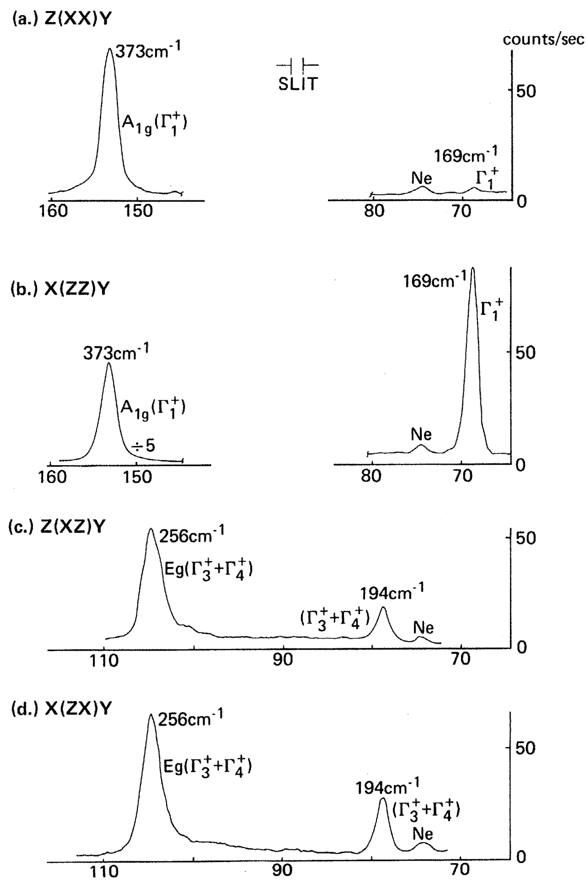


FIG. 2. Polarized spectra of single-exciton light scattering in $CoF_2$ at 2°K. Also shown are the strongest phonon lines $A_{1g}(\Gamma_1^+)$ and $E_g(\Gamma_3^+ + \Gamma_4^+)$. The relative intensities of the peaks have not been corrected for the polarization response of the spectrometer, but this correction has been made in Table I. Note that the gain used for the $A_{1g}(\Gamma_1^+)$ line in (b) is $\frac{1}{5}$ that in all the other spectra. As in Fig. 1, the energy scale is linear in the wavelength shift from 6328 Å. An approximate cross-section calibration was made relative to the 992-$\text{cm}^{-1}$ line of benzene (see Table I).

Ishikawa and Moriya[5] have recently calculated the these matrix elements of the orbital-dependent polarizability for $CoF_2$ under the assumption that the odd-parity states $E_u$ are $3d^6 4p$ and $3d^6 4f$ cobalt levels at ~$10^5$ $\text{cm}^{-1}$. There are lower lying charge-transfer states around $5\times10^4$ $\text{cm}^{-1}$,[11] but this assumption should give a good order of magnitude for the absolute extinction coefficient (or equivalently the cross section). The basis states for $|0\rangle$ and $|n\rangle$ were obtained from an effective Hamiltonian calculation within the $^4T_1$ term. The dipole operator couples the orbital parts of the $3d^7\,{}^4T_1$ states $|0\rangle$ and $|n\rangle$ directly to the odd-parity states $|u\rangle$ without the need for spin-orbit coupling (although, of course, spin-orbit coupling helps determine the linear combinations of $^4T_1$ states in $|0\rangle$ and $|n\rangle$). This is in contrast to the mechanism for scattering from spinlike excitations such as in $FeF_2$.

The results of this theory are compared with the experimental values in Table I. We have used Ishikawa and Moriya's[5] results and evaluated the cross sections for the He-Ne laser frequency, including the frequency dependence of the polarizability. The agreement is very satisfactory, particularly with regard to the relative cross sections, and supports their model. Further improvement could be obtained by carrying out the sum in Eq. (3) over the odd-parity states $E_u$ experimentally observed in $CoF_2$,[17] and by using better values for $\langle 0|P_{\mu,\nu}|u\rangle$ which in the present case have all been taken as 2.5 D. The main anomaly is in the ratio of the $XX$ to $YY$ intensity for the $\Gamma_1^+$ exciton which is observed to be very low.

We have not yet observed the two-particle scattering (two-magnon, two-exciton or exciton-magnon) and can set an upper limit for $dh/d\Omega$ of

Table I. Summary of light scattering from magnetic excitations in $CoF_2$. Unless otherwise stated, measurements are at 2°K.

| Excitation Symmetry at k=0 | Energy ($cm^{-1}$) | Width[a] ($cm^{-1}$) | Scattering Geometry $\mu\nu$ | $dh/d\Omega$ - Expt.[b] ($10^{-9} cm^{-1}/sr$) | $dh/d\Omega$ - Theory[c] ($10^{-9} cm^{-1}/sr$) |
|---|---|---|---|---|---|
| Magnon $\Gamma_3^+ + \Gamma_4^+$ | 37.5±.5 | ≤2.0 | YZ | .13 | .5 |
| | | | ZX | .27 | 1.1 |
| Excitons $\Gamma_1^+$ | 169.0 | ≤2.0 | XX | .1 | 2.8 |
| | | | ZZ | 1 | 4.7 |
| $\Gamma_2^+$ | 204[d] | | YX | ≤.1 | 0.3 |
| $\Gamma_3^+ + \Gamma_4^+$ | 194 | ≤3.0 | YZ | .45 | 1.4 |
| | | | ZX | .60 | 2.5 |
| Phonons $(A_{1g})\Gamma_1^+$ | 373 | 4 | XX | 2 | |
| | | | ZZ | 5 | |
| $A_{1g}$[e] | 366 | 10 | XX | 1 | |
| | | | ZZ | 2 | |
| $(E_g)\Gamma_3^+ + \Gamma_4^+$ | 256 | 5 | YZ = ZY | 3 | |
| $E_g$[e] | 245 | 10 | YZ = ZY | 1.5 | |

[a]Spectral slit width = 2 $cm^{-1}$.
[b]Absolute values ±50 %; relative values ±20 %. For comparison, the 992-$cm^{-1}$ line of benzene has $dh/d\Omega = 25\times10^{-9}$ $cm^{-1}/sr$.
[c]Derived from Ishikawa and Moriya, Ref. 5.
[d]This energy obtained from neutron scattering, Ref. 5.
[e]At 290°K. See also Ref. 14.

~$10^{-10}$ $cm^{-1}/sr$ for these processes. This is again in contrast to scattering from spinlike excitations, where the two-magnon scattering is stronger than the one-magnon.[1]

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