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SPIN-WAVE AND EXCITON DISPERSION RELATIONS OF COBALT FLUORIDE

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The dispersion relations of spin waves have been observed in antiferromagnetic cobalt fluoride at 4.5°K using inelastic neutron-scattering techniques. Measurements have been made not only of the excitations within the ground-state Kramers doublet of the paramagnetic phase, but also of the excitations to the first excited doublet of the Co^{++} ion. Insofar as we are aware, the latter are the first measurements of exciton dispersion relations in a single crystal obtained by neutron scattering techniques. The results are shown to be in at least qualitative agreement with a theory incorporating Heisenberg exchange forces between the spins on neighboring Co^{++} ions and with the crystal field parameters deduced by Gladney.[1]

The electronic-energy-level diagram of Co^{++} is shown in Fig. 1. Each Co^{++} ion is surrounded by an almost exactly cubic array of fluorine ions. The crystal field[2] from these splits the ^4F atomic state to give the ground state as an orbital triplet Γ_4. The rhombic and axial distortions of the field give rise to effects of similar size to those of the spin-orbit splitting, and Gladney[1] has deduced the relevant crystal-field and spin-orbit parameters from measurements of the g values[3] and infrared spectra.[4] The Γ_4 state is then split into six Kramers doublets, the lowest pair of which are separated by a frequency of only 4.5×10^{12} cps, while the next state is considerably higher in energy. The exchange field in the antiferromagnetic state then further splits the Kramers doublets, giving the lowest four states labeled A, B, C, D in Fig. 1.

The crystal of CoF_2 was grown at a rate of 2 mm/h by the Stockbarger process in a graphite crucible. The powder was first dehydrated by heating in a platinum crucible in an air furnace to 700°C, with an admixture of ammonium hydrogen fluoride to oppose hydrolysis. On first growth, the cone of the crystal was usually covered with a thin skin of cobalt, which could be peeled away before recrystallization. On regrowth, much less metal was formed, but it accumulated at the extreme tip of the

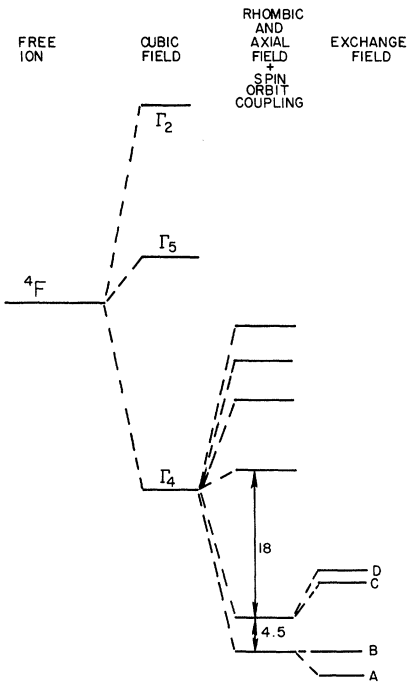

FIG. 1. The electronic-energy-level diagram of Co^{++} in CoF_2. The frequencies between the lowest three Kramers doublets are given in units of 10^{12} cps.

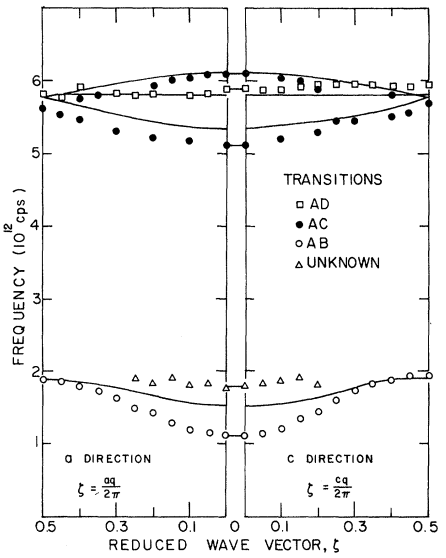

FIG. 2. The dispersion curves of magnetic excitations in CoF_2 at 4.5°K. The solid lines are theoretical calculations and the points are experimental results. The errors on measurements of the two low- and three high-frequency branches are typically about 0.03 and 0.15 (10^{12} cps), respectively.

cone and was often associated with gas bubbles. This was unfavorable for the growth of single crystals. However, by using a graphite mold inside the main crucible, drilled with four tapered cavities with cone-shaped ends, each connected through a small hole to a sump in the cone of the outer crucible, it was possible to segregate and maintain a single orientation in each cavity.

The single crystal (4 cm long and 1 cm diameter) was then placed in a metal cryostat with a (010) axis vertical, and the spin waves propagating along the [100] and [001] directions were observed by inelastic-neutron-scattering techniques. The triple-axis crystal spectrometer at the C5 facility of the NRU reactor at Chalk River Nuclear Laboratories was used throughout in its "constant Q" mode of operation.[5] The results are shown in Fig. 2 for the spin-wave or exciton modes associated with transitions between the states AB, AC, and AD of Fig. 1.

The results for $q=0$ are compared with the far-infrared peaks obtained by Richards,[6] Barker and Ditzenberger,[7] and Allen[8] in Table I. Our results are in excellent agreement with the strong modes in the infrared spectrum which are labeled as modes 2 and 8 of Table I. Mode 1 is not observed in our experiments. Since the frequency of mode 6 is close to twice the AB zone-boundary frequency observed in the present experiment, it is possible that the mode arises from two-magnon processes similar to those observed by Allen, Loudon, and Richards in MnF_2.[9] Mode 7 has been observed by us, and we have also detected mode 9, which is not observed in the infrared spectrum because it is obscured by a strong lattice-mode absorp-

Table I. The frequencies, in 10^{12} cps, of the $q=0$ magnetic excitations in CoF_2 as determined by these measurements and by far-infrared measurements.

Label	Neutron measurement	Far-infrared measurement	Reference
1		0.855 ± 0.002	6
2	1.11 ± 0.02	1.08 ± 0.01	6
3	1.79 ± 0.03	1.86	7
4		2.00	6 quoted by 8
5		2.13	6 quoted by 7
6		3.60	7
7	5.1 ± 0.1	5.055	8
8	5.87 ± 0.1	5.797	7,8
9	6.11 ± 0.15		
10		6.96	7
11		7.68	8
12		8.25	8

tion.[7] Modes 10 and 12 arise possibly from interaction with phonons of similar frequency,[7] while mode 11 may be the result of a two-magnon process involving simultaneously an AB and AD transition. We shall discuss modes 3, 4, and 5 later.

The modes AD and AC were distinguished by comparing the intensities of the neutron groups obtained when the momentum transfer Q was along the [100] and [001] directions. For small Q, the intensity for neutron scattering by magnetic excitations is proportional to[10]

$$\langle\psi_F|\vec{L}_\perp+2\vec{S}_\perp|\psi_I\rangle,$$

where ψ_F is the excited state, ψ_I is the initial state, and $\vec{L}_\perp$ and $\vec{S}_\perp$ are the components of the orbital and spin angular momentum, $\vec{L}$ and $\vec{S}$, respectively, which are perpendicular to $\vec{Q}$. The wave functions in the Γ_4 manifold can be written as linear combinations of the form $|1_z, S_z\rangle$. (1_z is the component of the effective $L=1$ quantum number in the Γ_4 manifold,[11] and $1=-\frac{3}{2}L$.) The state A and C may then be written as a linear combination of the states $|\pm1,\frac{3}{2}\rangle$, $|0,\frac{1}{2}\rangle$, $|\pm1,-\frac{1}{2}\rangle$, and $|0,-\frac{3}{2}\rangle$, while B and D are correspondingly given by $|0,\frac{3}{2}\rangle\cdots$, etc. The operators L_x+2S_x and L_y+2S_y connect state A with states B and D, while L_z+2S_z connects A with C. Consequently, if $\vec{Q}$ is approximately along [001], only the AB and AD branches are observed, while with $\vec{Q}$ along [100], all three branches are obtained.

Also shown in Fig. 2 are theoretical calculations of the spin-wave spectra of CoF_2. The calculations which will be described in detail in a later publication are based on Gladney's[1] crystal-field parameters and an exchange constant of 0.118×10^{12} cps between next-nearest neighbor spins. The results clearly give very reasonable agreement with the experimental results for the AB, AC, and AD transitions but fail to account for the unknown branch. Work is in progress both to study the temperature dependence of these excitations and to study the nature of the unknown branch, and will be reported later.

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