Excitations of isolated clusters of Co^{2+} magnetic ions in $KZn_{0.92}Co_{0.08}F_3$

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(Received 16 July 1984)

Inelastic neutron scattering from clusters of Co^{2+} ions in cubic $KZnF_3$ is reported. From measurements of the lowest pair mode at (1.676±0.008) THz, we find that the exchange between Co^{2+} ions is surprisingly isotropic, with any bond anisotropy being less than 2.4%. An accurate value of the isotropic exchange parameter has been obtained [$J=(0.330\pm0.005)$ THz] free of the many-body effects that complicate the interpretation of exchange coupling in concentrated crystals. Neutron scattering was also observed from triplet and quartet states at (2.47±0.02) and (1.09±0.05) THz, respectively, and a higher-frequency pair state at 8.8 THz. The results are interpreted in terms of an elementary theory of cluster spectra for ions with nonzero angular momentum.

I. INTRODUCTION

The interactions between magnetic ions, free of many-body effects, may be determined from studies of the spectrum of spin transitions of pairs of adjacent magnetic ions. Studies of magnetic pairs have conventionally been carried out by electron paramagnetic resonance[1] at megahertz frequencies, where the spectrum is determined indirectly from the temperature dependence of the various resonances belonging to different magnetic pair states. Recently, we have shown how neutron scattering may be used to directly observe the spectrum of pair transitions.[2,3] Related studies on complex organic material have been carried out.[4] In general, it is found that the accuracy with which the dominant exchange coupling is determined is greater than the accuracy of most resonance experiments.

The spin coupling between ions carrying orbital angular momentum, such as Co^{2+} ions, is of particular interest because of possible bond anisotropy, as discussed by Elliott and Thorpe.[5] Copland and Levy,[6] whose calculations were actually for direct exchange rather than superexchange, also predicted a 5–10% exchange anisotropy that depended on the spin-orbit state occupied by the ions.

In this paper we describe the results of a neutron-scattering study of the spin-excitation spectra of isolated pairs, triplets, and quartets of Co^{2+} ($L=3$, $S=\frac{3}{2}$) magnetic ions randomly substituted for 8% of the nonmagnetic Zn^{2+} ions in the $KZnF_3$ perovskite lattice. The elementary theory of cluster spectra, first developed for our experiments on clusters of pure spin Mn^{2+} ions,[2,3] is extended in Sec. II to exchange-coupled ions of nonzero angular momentum in the presence of spin-orbit coupling. The latter coupling affects the ground multiplet directly as well as indirectly by second-order mixing of excited states.[7] The experimental results for pair, triplet, and quartet excitations at 4.2 and 77 K, as well as for relevant phonons, are presented in Sec. III. In Sec. IV we discuss, in particular, the principal unexpected finding of this study, namely that the exchange coupling two Co^{2+} ions in their $j=\frac{1}{2}$ Kramers ground states is isotropic to within the resolution linewidth of the spectrometer, and is certainly smaller than the 10% anisotropy predicted in theoretical calculations for Co^{2+} ions.

II. SPIN EXCITATIONS OF CLUSTERS OF IONS HAVING ORBITAL ANGULAR MOMENTUM

The effective Hamiltonian for a single Co^{2+} ion with first- and second-order spin-orbit coupling within the effective $l=1$ and $S=\frac{3}{2}$ multiplet is[7–9]

$$H_1=\lambda'\vec{l}\cdot\vec{S}+\kappa(\vec{l}\cdot\vec{S})^2+\rho(l_x^2S_x^2+l_y^2S_y^2+l_z^2S_z^2)\ . \tag{1}$$

As usual, we treat the motion of the $L=3$ orbital angular momentum within the cubic-crystal-field $^4T_1$ ground state in terms of an $l=1$ effective angular momentum operator with $\vec{L}=\alpha\vec{l}$, where $\alpha\approx-\frac{3}{2}$. There may also be orbital reduction due to covalency or the dynamic Jahn-Teller effect,[10] but all such effects are included in the renormalized values of λ', κ, and ρ determined from experiment. In the absence of exchange and for isotropic spin-orbit interaction ($\rho=0$), the 12 states of the ground-state multiplet may be characterized by values of $\vec{j}=\vec{l}+\vec{S}$ of $\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$, as is shown in Fig. 1. The terms in κ and ρ change the spacings of the ground $^4T_1$ spin-orbit multiplet from the Landé interval rule and split the $j=\frac{5}{2}$ spin-orbit level.

The Hamiltonian for a cluster of ions coupled by the dominant nearest-neighbor interaction of the perovskite lattice is then

$$H=\sum_{i,j}J^{\perp}\vec{S}(i)\cdot\vec{S}(j)+(J^{\parallel}-J^{\perp})[\vec{S}(i)\cdot\hat{R}(i,j)][\vec{S}(j)\cdot\hat{R}(i,j)]+\sum_i H_1(i)\ , \tag{2}$$

where $\hat{R}(i,j)$ is the unit vector between ions i and j of the cluster, and $J^{\parallel}$ and $J^{\perp}$ are the spin-coupling strengths for spin components parallel and perpendicular to the bond.

A. Pair spectra

The solution of the full coupled-pair problem was obtained by evaluating the matrix elements of Eq. (2) between the $(2l+1)^2\times(2S+1)^2=144$ pair states of the two ions of the form

$$|X\rangle=|l_z(1)S_z(1)\rangle\,|l_z(2)S_z(2)\rangle\ .$$

The resultant 144×144 matrix was diagonalized to give the exact energies E_n and eigenfunctions

$$|n\rangle=\sum_X U(n,X)\,|X\rangle\ .$$

The neutron scattering, $S(\vec{Q},\Omega)$, is proportional to the sum of the magnetic dipole strengths of each transition:

$$S(\vec{Q},\Omega)=\sum_{\alpha}(1-\hat{Q}_{\alpha}^{2})\sum_{n,m}\frac{e^{-\beta E_n}}{Z}\left|\sum_i e^{i\vec{Q}\cdot\vec{R}(i)}\langle m\,|M_{\alpha}(i)|\,n\rangle\right|^2\delta(\Omega-\Omega_{mn})\ , \tag{3}$$

where $\vec{M}=\mu_B(\vec{L}+2\vec{S})$ for small wave-vector transfer, $\vec{Q}$.

The scattering for pairs with bonds randomly oriented in the X, Y, or Z crystallographic directions was obtained by evaluating the matrix element of $\vec{M}$ in Eq. (3) for a single pair whose bond lies along the Z direction, and then summing the result for all values of $\vec{Q}$ related by cubic-symmetry operations. With the parameters of Table I, the single-ion and pair spectra of Fig. 1 are obtained. These parameters are approximately the same as those[11] for $KCoF_3$ ($\lambda'=6.24$ THz, $J=0.311$ THz).

An effective $j=\frac{1}{2}$ model with Hamiltonian

$$\sum_{i,k}J_{1/2}\,\vec{j}(i)\cdot\vec{j}(k)$$

was developed which reproduced the pair levels arising from the Co^{2+} ground doublet. Denoting the effective isotropic exchange constant by $J_{1/2}$, the lowest pair frequency is then given by

$$\nu_{\text{pair}}=2J_{1/2}\ . \tag{4}$$

Since the full theory above gives $\nu_{\text{pair}}=1.68$ THz$=5.09J$, where J is the isotropic exchange between true spins, it follows that

$$2J_{1/2}=5.09J\ ,$$

or

$$J_{1/2}=0.84\text{ THz}\ . \tag{5}$$

For a pair of Co^{2+} ions, the strengths of the various transitions observable in neutron scattering, proportional to the square of the magnetic-dipole-transition matrix element as in Eq. (3), have also been evaluated and are shown in Fig. 1.

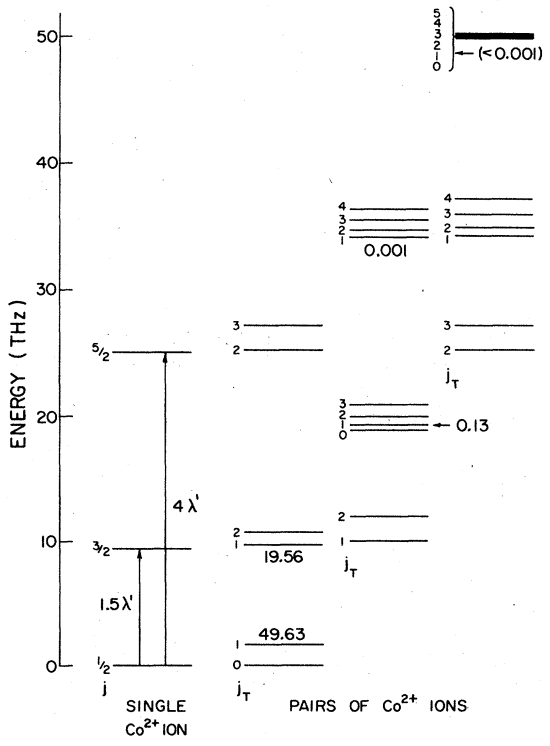

FIG. 1. Low-lying energy levels for single Co^{2+} ions and pairs of Co^{2+} ions with the exchange- and spin-orbit-coupling parameters given in Table I. For the pair spectrum the relative intensities at the wave vector $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ for transitions from the ground state are given if they are nonzero. The total effective angular momentum of the pair is $j_T=\sum_{i=1}^{2}[l(i)+S(i)]$.

TABLE I. Isotropic spin-orbit and exchange coupling for Co^{2+} ions in $KZnF_3$.

Parameter	Value (THz)
λ'	6.24
$\kappa=\rho$	0
$J^{\parallel}=J^{\perp}=J$	0.33
ν_{pair}	1.68

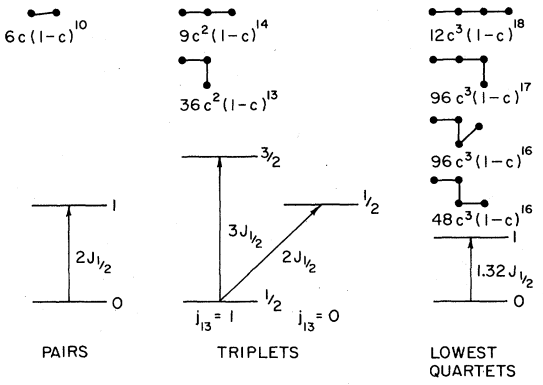

FIG. 2. Level schemes and cluster probabilities within the effective $j=\frac{1}{2}$ model for pairs, triplets, and open quartets. The transition frequencies are given in terms of the effective coupling parameters $J_{1/2}$ in the effective $j=\frac{1}{2}$ model. The total spin, $j_t=\sum_i j(i)$, for each level is given, and for the triplet scheme each band is described by the additional spin quantum number $j_{13}=j(1)+j(3)$.

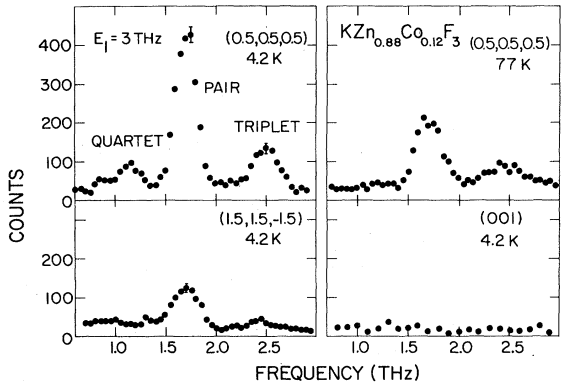

FIG. 3. Neutron scattering from pairs [(1.676±0.008) THz], triplets [(2.47±0.02) THz], and quartets [(1.09±0.05) THz] of Co^{2+} ions in $KZn_{0.92}Co_{0.08}F_3$ at several wave-vector transfers normalized to the same number of incident neutrons. (a) and (c) demonstrate the form-factor dependence of the intensity. (b) shows the rapid intensity reduction upon raising the temperature. (d) illustrates the absence of neutron scattering at a zero in the structure factor.

B. Triplet and quartet spectra

Having established that the lowest pair transition is well described by coupling two $j=\frac{1}{2}$ states, we can write an effective $j=\frac{1}{2}$ Hamiltonian for larger clusters, thus reducing the dimension of the matrix for the N-atom cluster from 12^N to 2^N. In Fig. 2 we show the spectra of three isotropically coupled $j=\frac{1}{2}$ ions and the spectrum of an open cluster of four $j=\frac{1}{2}$ ions, i.e., one which does not close on itself so that ion 1 does not couple to ion 4. In practice, these results were obtained from the same program that was used to calculate the exact pair spectra for two $l=1$, $S=\frac{3}{2}$ ions by first setting $\kappa=\rho=0$ and then taking

$$l(1)=S(1)=l(2)=S(2)=\tfrac{1}{2}=j\ .$$

The quartet states are then generated by choosing $\lambda(1)=2J_{1/2}=\lambda(2)$, and, for the triplet, $\lambda(1)=2J_{1/2}$ but $\lambda(2)=0$. This procedure follows from the fact that the spin-orbit and exchange interactions have the same isotropic form.

The main triplet mode ($\Delta j_T=1$, $\Delta j_{13}=0$) is calculated to occur at $3J_{1/2}=2.52$ THz with a cross-band transition ($\Delta j_T=0$, $\Delta j_{13}=-1$) at $2J_{1/2}$. Thus, in an experiment, one triplet peak lies under the much stronger pair peak [Eq. (4)]. The main quartet mode ($\Delta j_T=1$) is calculated to lie at $1.32J_{1/2}=1.11$ THz.

III. RESULTS AND DISCUSSION

Measurements were made of the inelastic neutron scattering from a single crystal of $KZn_{1-c}Co_cF_3$ approximately 80 mm×20 mm×20 mm in size. The concentration of Co^{2+} ions was measured using flame atomic absorption spectroscopy. The crystal proved to have a concentration gradient, with $c=0.125$ at the initial growth end and $c=0.025$ at the other end of the boule. The average fraction of Co^{2+} ions was thus taken to be $c=0.075$. The N5 triple-axis spectrometer at the NRU reactor, Chalk River, was operated in the constant-Q mode with constant scattered neutron energy $E1$. The 3-cm-wide incident beam was produced by a Ge(113) monochromator, and the scattered neutron energy was determined by a (002) graphite analyzer. Collimation was 0.7° before and 1.0° after the specimen, with $E_1=3$ THz for most runs. For high-resolution runs with $E_1=1.6$ THz, the collimation after the specimen was 0.7°.

Typical results are shown in Fig. 3. At 4.2 K, three peaks were observed whose frequencies [(1.09±0.05), (1.676±0.008), and (2.47±0.02) THz, respectively] were independent of wave vector, as expected for the excitations of isolated clusters. The intensities of the peaks fall with $|\vec{Q}|$ (lower left-hand panel of Fig. 3), in agreement with the square of the Co^{2+} magnetic form factor.

A. Pairs

The spectrum is dominated by the peak at 1.68 THz. It arises from the $j_T=0\rightarrow j_T=1$ ground transition of pairs of Co^{2+} ions (Fig. 1). This assignment is supported by the fact that the frequency of the pair transition, with the full level scheme (Fig. 1) but with the isotropic exchange constant, $J=0.31$ THz, of $KCoF_3$,[11] is calculated to be 1.58 THz.

From Fig. 3 it is seen that the intensity of the pair mode shows a dramatic variation with wave vector. It vanishes at the nuclear zone center (0,0,1) and is strongest at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, the wave vector which becomes the antiferromagnetic zone center) of pure $KCoF_3$. This wave vector corresponds to putting adjacent magnetic ions in antiphase, and hence favors strong scattering from ions that are antiferromagnetically coupled. The cross section for the $0\rightarrow1$ transition for a pair of identical antiferromagnetically coupled ions of any spin is readily shown to be of the form

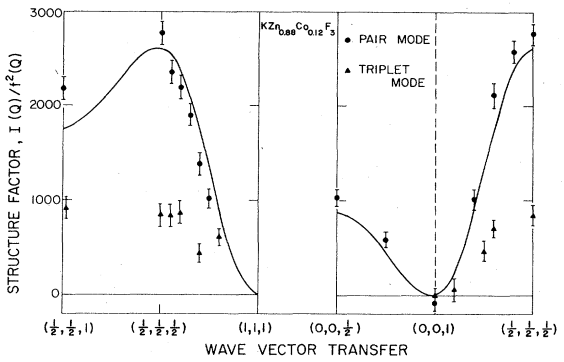

FIG. 4. Structure factor (integrated intensity divided by the form factor) of the pair (solid circles) and $3J_{1/2}$-triplet (solid triangle) modes as a function of wave-vector transfer. The solid curve represents the theoretical structure factor for pair modes, Eq. (6), and is normalized to the 4.2-K experimental results near the peak of the structure factor.

$$I(\vec{Q})=f^2(\vec{Q})[\sin^2(aQ_x/2)+\sin^2(aQ_y/2)+\sin^2(aQ_z/2)] \ . \tag{6}$$

For comparison with this prediction, the integrated intensity of the pair mode was carefully measured as a function of $\vec{Q}$, with the result shown in Fig. 4. In view of the difficulties of measuring neutron intensities, which may be severe in the presence of the cobalt nuclear absorption cross section in an irregularly shaped crystal, the agreement between theory and experiment is more than adequate.

Upon heating to 77 K the pair-mode frequency decreases slightly to (1.65±0.01) THz (a shift of this size would not be inconsistent with the change in exchange resulting from thermal expansion), but its intensity decreases greatly, as is shown in the top right-hand panel of Fig. 3. The ground-state population is calculated to fall from 1.00 to 0.49 between 4.2 and 77 K. The integrated intensity is observed to fall to 0.54±0.10, in excellent agreement with calculation. Less clearly understood is the increase in width of the pair peak from a resolution-limited value of (0.25±0.02) THz at 4.2 K to (0.31±0.03) THz at 77 K. The increase is small, barely exceeding the combined experimental errors, but, since it was observed in other scans, it is believed to be a real effect. One mechanism for the increased width could be broadening of the localized excitation caused by coupling to pairs of phonons. At low temperatures, only phonon creation is possible and the phase space available from the parts of the acoustic-phonon branches whose frequencies are less than the pair-mode frequency is small. At high temperatures, simultaneous phonon absorption and emission is possible, which permits the much larger phase space of the higher-frequency phonon modes to be involved.

B. Triplets and quartets

The peak at 2.47 THz in Fig. 3 is assigned on the basis of its frequency and intensity to triplets, and that at 1.09 THz to quartets.

The triplet mode exhibits a cross section that is significantly different from that of the pair (Fig. 4). The $3J_{1/2}$-triplet cross section at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is observed to be 0.33 of the cross section for the peak at $2J_{1/2}$. Fortunately, there is no contribution at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ to the $2J_{1/2}$ intensity from triplets since the theoretical cross section for the triplet transition at $2J_{1/2}$ falls to zero at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, basically because spins 1 and 3 precess in phase. The ratio of the numbers of triplets per unit volume to the number of pairs per unit volume for a crystal containing a concentration c of magnetic impurities is

$$9c^2(1-c)^{14}+36c^2(1-c)^{13}:6c(1-c)^{10} \ , \tag{7}$$

i.e., 0.44 for $c=0.075$. We show in the Appendix that the ratio of the $3J_{1/2}$-triplet cross section to the $2J_{1/2}$-pair cross section is 32/9:2, or 1.78. Thus the observed intensity ratio between the triplet and pair peaks, given by the product of their relative concentration and cross section, is predicted to be 0.78. This is in fair agreement with the observed ratio of 0.33.

C. Phonon pair-mode coupling

The measurements in the $[\zeta\zeta\zeta]$ direction of the cluster frequencies and of the phonon frequencies that lie nearby are shown in Fig. 5. A careful search was made for spin-phonon coupling affecting the pair mode, but none was found. This is perhaps surprising in view of the strong magnon-phonon coupling observed by Holden *et al.*[12] in $KCoF_3$ between the lowest magnon and the TA phonon near the R point. If spin-phonon coupling occurs, there should be scarcely any effect on the phonons as only 12% of the ions are magnetic, but the effect on the cobalt local mode should be measurable as each Co^{2+} ion can couple to the phonons, producing local displacements of the appropriate symmetry. There may therefore be shifts in the frequencies of the cluster modes because of spin-phonon coupling, but the shift is independent of wave vector because the magnetic modes are localized. The coupling is thus hard to observe because it provides no unique signature, such as the anticrossing characteristic of the coupling of magnon and phonon in systems where both exci-

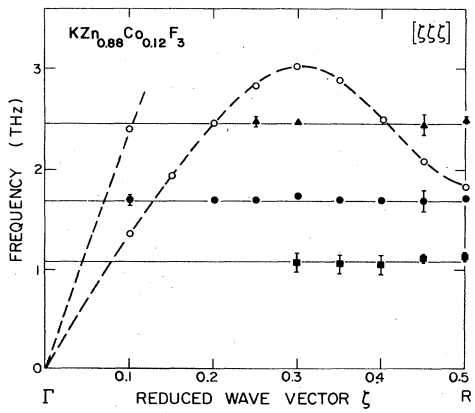

FIG. 5. Dispersion relation for acoustic phonons (open circles) and pair (solid circles), triplet (solid triangles), and quartet (solid squares) magnetic excitations in the $[\zeta\zeta\zeta]$ direction in $KZn_{0.92}Co_{0.08}F_3$ at 4.2 K.

tations exhibit dispersion. Because Co^{2+} is a Kramers ion, the coupling only exists in the ordered phase of $KCoF_3$ through mixing higher states with the ground state in the exchange field.[11] As the exchange splitting of the pair is less than 4 times the exchange splitting of the ground state in $KCoF_3$, we estimate that any frequency shift induced by a linear coupling to the phonons does not exceed one-fourth that of the magnon-phonon—interaction energy of 0.35 THz for $KCoF_3$,[12] and is therefore less than 0.1 THz.

D. Exchange anisotropy

The results at $E_1=3$ THz (Fig. 3) show no evidence of the bond anisotropy in the exchange constant predicted by Elliott and Thorpe.[5] The effect of having $J^{\parallel}\neq J^{\perp}$ in Eq. (2) is to split the $j_T=1$ first-excited level of the pair into a singlet and doublet. Measurements at higher resolution obtained with $E_1=1.6$ THz, and with 0.7° collimation before and after the specimen, were therefore carried out to set limits on any splitting of the pair mode. The results exhibited in Fig. 6 show a single symmetric peak of full width at half maximum (0.079±0.008) THz. Thus no broadening over and above the instrumental resolution, calculated to be 0.08 THz, was observed. As an anisotropy splits the transition in a 2:1 intensity ratio, the symmetry of the line suggests that any splitting is less than 0.04 THz. We conclude that, to be consistent with the observed width and symmetrical shape of the pair peak, the apparent exchange between Co^{2+} ions in their ground doublet states is isotropic to better than 2.4%. This sets an upper bound on anisotropy in the $j=\frac{1}{2}$ states which is 4 times lower than was possible in an earlier search for bond anisotropy in $KCoF_3$.[12]

E. Exchange constants

The results for the pair transition at high resolution lead to the most accurate value for its frequency. All the cluster frequencies are tabulated in Table II, where they are compared with theoretical predictions based on the isotropic exchange parameter that best describes the pair frequency when the full level scheme is used.

F. High-frequency scattering

The isotropy of the exchange interactions observed within $j=\frac{1}{2}$ states does not imply that the full exchange is isotropic. Certain forms of anisotropic interaction can vanish within a $j=\frac{1}{2}$ manifold, within which only operators O_1^m have nonzero matrix elements. Thus quadrupole forms are excluded, at least in the limit of weak exchange fields. It may be much easier, however, to observe the effects of anisotropy in transitions involving the $j=\frac{3}{2}$ or $\frac{5}{2}$ levels, since operators O_n^m with n up to $2j+1$ can be important. The $j=\frac{1}{2}\rightarrow j=\frac{3}{2}$ transition is within a frequency range that is reasonably accessible to neutron scattering, and a search was carried out for the pair modes associated with this transition.

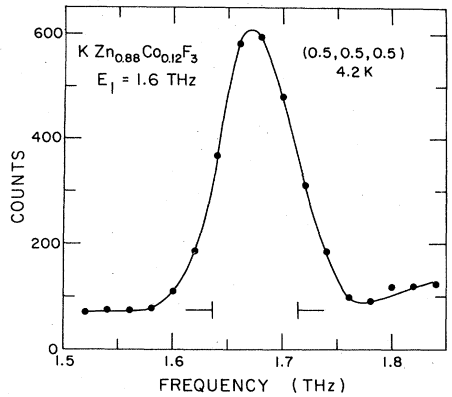

FIG. 6. High-resolution constant-Q measurement of the pair mode at the peak of the structure factor. The frequency resolution (0.08 THz) is 3 times lower than that of the scans in Fig. 3.

Neutron groups were observed at (8.8±0.2) and (10.0±0.2) THz at many different wave vectors (Fig. 7). The wave-vector dependence of the scattering (lower right-hand panel of Fig. 7 in addition to results at other pairs of equivalent wave vectors) suggests that both groups are predominantly magnetic. From the level scheme corresponding to the parameters of Table I, the single-ion transition is calculated to be 9.36 THz and the allowed pair transition is 9.65 THz. A splitting of 0.3 THz would be unresolved at this frequency transfer, so that it is probable that the observed peak at 8.8 THz is the sum of the single-ion and pair-mode transitions. The Raman scattering results[13] for crystals with lower cobalt-ion concentrations show that the $j=\frac{1}{2}$ to $j=\frac{3}{2}$ single-ion transition does occur at 8.8 THz. The group at 8.8 THz increases in intensity as the wave vector increases from (1,1,1) to (1.25,1.25,1.25) like the structure factor of a pair mode [Eq. (6)], but has appreciable intensity at (0,0,2), where Eq. (6) predicts zero intensity. The remaining intensity at this wave vector is attributed to the single-ion transition whose structure factor is independent of wave vector. The intensity of the group at 8.8 THz decreases

TABLE II. Comparison of calculated and experimental frequencies for low-lying transitions within clusters of Co^{2+} ions in $KZnF_3$.

Type of mode	Frequency in full level scheme ($J=0.33$ THz)	Frequency in $j=\frac{1}{2}$ description ($J_{1/2}=0.84$ THz)	Calculated frequency (THz)	Measured frequency (THz)
Pair	$5.09J$	$2J_{1/2}$	1.68	1.676±0.008
Triplet		$2J_{1/2}$	1.68	
Triplet		$3J_{1/2}$	2.52	2.47 ±0.02
Quartet		$1.32J_{1/2}$	1.11	1.09 ±0.05

slightly and its width increases upon raising the temperature from 4.2 to 77 K. This result is consistent with populating the first-excited pair mode at 1.68 THz and exciting the two lowest j_T (Fig. 1) states by neutron energy loss at frequencies which lie just below and above the ground-state transition.

From the neutron-inelastic-scattering measurements of Lehner *et al.*,[14] and the optical work of Perry and Young,[15] Γ-point optical phonons are observed in $KZnF_3$ at 8.75 THz (LO) and 12.1 THz (TO). The proximity of the observed magnetic peak at 8.8 THz and the LO mode at Γ is thought to be coincidental since the observed peak is wave-vector independent, and the R-point frequencies, for example, of the LO and TO modes, are 8.0 and 9.5 THz, respectively.

The frequency, 8.8 THz, for the $j=\frac{1}{2}$ to $j=\frac{3}{2}$ transition is well reproduced if one uses, for Eq. (1), the parameters that fit the two Raman transitions[13] rather than the effective isotropic spin-orbit parameter $\lambda'=6.24$ THz used earlier in this paper and originally determined from neutron experiments in $KCoF_3$.[12] The parameters $\lambda'=7.93$ THz, $\kappa=0.09$ THz, and $\rho=1.44$ THz obtained from the fit to the Raman data give the single-ion ($j=\frac{1}{2}$ to $j=\frac{3}{2}$) frequency to be 8.80 THz and the pair-mode frequencies to be 9.10 and 9.37 THz (Table III).

The group at 10.0 THz is not fully understood at present, although several possible explanations of its existence can be given. It is certain, however, from its frequency, its lack of a structure factor, and its approximate form-factor dependence, that it is not a phonon. It does not have a structure factor characteristic of a pair mode; for example, its intensity decreases between (1,1,1) and (1.25,1.25,1.25). The possible explanations are (a) the triplet analog of the pair excitation at 8.8 THz, (b) phonon incoherent scattering seen via the paramagnetic Co^{2+} scattering cross section, (c) pair transitions involving $j_T=0$ to $j_T=2$ states which come 0.8 and 1.5 THz above the $j_T=0$ to $j_T=1$ ground-state transition, and (d) a complex interaction with an optical phonon mode such that only the magnetic part of the cross section is observed. If possibility (b) holds, it seems surprising that the incoherent paramagnetic vibrational scattering does not appear to contribute at low frequencies. Option (c) would require that the selection rule $|\Delta_j|=1$ be broken, and a quadrupolar interaction would be needed to effect this.

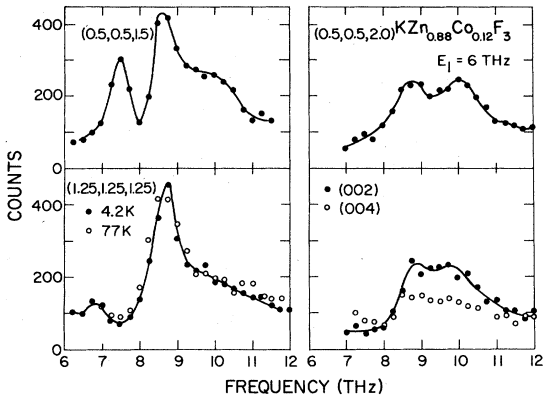

FIG. 7. High-frequency scattering in $KZn_{0.92}Co_{0.08}F_3$ at 4.2 K unless otherwise indicated. The modes at (0.5,0.5,1.5) at 7.5 THz and (1.25,1.25,1.25) at 6.85 THz are phonon excitations. The scattering at frequencies larger than 8 THz has two components centered on 8.8 and 10.0 THz and is predominantly, but not completely, magnetic.

IV. SUMMARY

From neutron-scattering measurements of the transition frequencies of pairs, triplets, and quartets of Co^{2+} ions in $KZnF_3$, we have shown that the exchange between Co^{2+} ions is surprisingly isotropic, any bond anisotropy being less than 2.4%. An accurate value of the isotropic exchange parameter $J=(0.330\pm0.005)$ THz has been ob-

TABLE III. Calculated single-ion and pair transition frequencies, ν, and neutron scattering intensity, I, at the wave vector $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and 4.2 K for the model with second-order spin-orbit interaction ($\lambda'=7.93$ THz, $\kappa=0.09$ THz, and $\rho=1.44$ THz). The observed Raman frequencies of Ref. 13 used to obtain the spin-orbit parameters are also given.

	Single-ion transitions			Pair transitions $j_T=0$ to $j_T=1$	
Assignment	Raman frequency (THz)	ν (THz)	I	ν (THz)	I
		$j=\frac{1}{2}$ to $j=\frac{1}{2}$			
Γ_6^+ to Γ_6^+	0	0	11.0	1.67	47.3
		$j=\frac{1}{2}$ to $j=\frac{3}{2}$			
Γ_6^+ to $^{(1)}\Gamma_8^+$	8.78	8.81	13.6	9.10	19.0
				18.11	0.1
				19.78	<0.01
		$j=\frac{1}{2}$ to $j=\frac{5}{2}$			
Γ_6^+ to $^{(2)}\Gamma_8^+$	28.48	28.60	<0.01	32.23	0.03
Γ_6^+ to Γ_7^+	31.03	31.12	0.02	38.03	<0.01
				40.35	<0.01

tained, free of the many-body effects that complicate the interpretation of exchange coupling in concentrated crystals.

APPENDIX: TRIPLET AND PAIR ENERGIES AND TRANSITION STRENGTHS

For an isolated triplet of Co^{2+} ions interacting via an isotropic, effective $j=\frac{1}{2}$ Hamiltonian,

$$H=2J_{1/2}[\vec{j}(1)\cdot\vec{j}(2)+\vec{j}(2)\cdot\vec{j}(3)]\ , \tag{A1}$$

the eigenvalues may be obtained by defining a total spin $\vec{j}_T=\vec{j}_1+\vec{j}_2+\vec{j}_3$ and a pair spin $\vec{j}_{13}=\vec{j}_1+\vec{j}_3$ to write

$$H=J_{1/2}[j_T(j_T+1)-j_{13}(j_{13}+1)-j(j+1)]\ , \tag{A2}$$

with solutions

$$\begin{aligned} &E=-2J_{1/2} \quad \text{for } j_T=\tfrac{1}{2},\ j_{13}=1\ , \\ &E=+J_{1/2} \quad \text{for } j_T=\tfrac{3}{2},\ j_{13}=1\ . \end{aligned} \tag{A3}$$

To calculate transition strengths, we introduce Ising basis states. The ferromagnetic state $|1,1,1\rangle$ is related by a spin flip to the antiferromagnetic states $|1,-1,1\rangle$, $|-1,1,1\rangle$, and $|1,1,-1\rangle$, and the ferromagnetic state $|-1,-1,-1\rangle$ is similarly related to the states $|-1,1,-1\rangle$, $|1,-1,-1\rangle$, and $|-1,-1,1\rangle$. The problem therefore splits into two coupled time-reversed spaces. Within the first space the ferromagnetic state $|1,1,1\rangle$ at $J_{1/2}$ is not coupled to any other, and the spin-flip states are described by a matrix Hamiltonian

$$\begin{array}{c} \\ |1,-1,1\rangle \\ |-1,1,1\rangle \\ |1,1,-1\rangle \end{array} \begin{array}{c} \begin{array}{ccc} |1,-1,1\rangle & |-1,1,1\rangle & |1,1,-1\rangle \end{array} \\ \begin{pmatrix} -J_{1/2} & J_{1/2} & J_{1/2} \\ J_{1/2} & 0 & 0 \\ J_{1/2} & 0 & 0 \end{pmatrix} \end{array} .$$

The eigenvalues λ and wave functions of the four states of the first space are thus

$$\begin{aligned} &\lambda=-2J_{1/2}\ , \\ &|g_+\rangle=\frac{(2|1,-1,1\rangle-|-1,1,1\rangle-|1,1,-1\rangle)}{\sqrt{6}}\ , \\ &\lambda=0,\quad |c_+\rangle=\frac{(|-1,1,1\rangle-|1,1,-1\rangle)}{\sqrt{2}}\ , \\ &\lambda=J_{1/2}\ , \\ &|b_+\rangle=\frac{(|1,-1,1\rangle+|-1,1,1\rangle+|1,1,-1\rangle)}{\sqrt{3}}\ , \\ &\lambda=J_{1/2},\quad |a_+\rangle=|1,1,1\rangle\ . \end{aligned} \tag{A4}$$

The neutron scattering involves matrix elements of the spin which allow transitions from the ground state $|g_+\rangle$ to the ferromagnetic state $|a_+\rangle$ of the same space, and to the antiferromagnetic excited state $|b_\pm\rangle$ of both spaces. The spin matrix elements for scattering at a nuclear point $(+)$ such as (1,1,1) and a magnetic point $(-)$ such as $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are then given, for the transition at $3J_{1/2}$, by

$$\begin{aligned} &\langle a_+|j_+(1)\pm j_+(2)+j_+(3)|g_+\rangle=\begin{bmatrix}0\\-2\sqrt{6}/3\end{bmatrix}\equiv\alpha_+\ , \\ &\langle b_-|j_-(1)\pm j_-(2)+j_-(3)|g_+\rangle=\begin{bmatrix}0\\2\sqrt{2}/3\end{bmatrix}\equiv\alpha_-\ , \\ &\langle b_+|j_z(1)\pm j_z(2)+j_z(3)|g_+\rangle=\begin{bmatrix}0\\-2\sqrt{2}/3\end{bmatrix}\equiv\alpha_z\ , \end{aligned} \tag{A5}$$

whereas those of the $2J_{1/2}$ transitions vanish. The total intensity of the six $3J_{1/2}$ transitions from the $|g_+\rangle$ and $|g_-\rangle$ ground states is then proportional to a spin structure factor,

$$\begin{aligned} I_3(3J_{1/2})&=2[(1+\hat{Q}_z^2)(\alpha_+^2+\alpha_-^2)/4+(1-\hat{Q}_z^2)\alpha_z^2] \\ &=\begin{bmatrix}0\\\frac{32}{9}\end{bmatrix}\ , \end{aligned}$$

independent of triplet configuration at these high-symmetry points, as well as proportional to the square of the form factor.

The pair Hamiltonian involves two pure ferromagnetic states, $|1,1\rangle$ and $|-1,-1\rangle$, at $J_{1/2}/2$, as well as the antiferromagnetic part

$$\begin{array}{c} \\ |1,1\rangle \\ |-1,-1\rangle \end{array} \begin{array}{c} \begin{array}{cc} |1,-1\rangle & |-1,1\rangle \end{array} \\ \begin{pmatrix} -J_{1/2}/2 & J_{1/2} \\ J_{1/2} & -J_{1/2}/2 \end{pmatrix} \end{array} ,$$

with solutions

$$\begin{aligned} &\lambda=-3J_{1/2}/2,\quad |g\rangle=(|1,-1\rangle-|-1,1\rangle/\sqrt{2}, \\ &\lambda=J_{1/2}/2,\quad |e_z\rangle=(|1,-1\rangle+|-1,1\rangle)\sqrt{2}, \\ &\qquad\qquad |e_+\rangle=|1,1\rangle, \\ &\qquad\qquad |e_-\rangle=|-1,-1\rangle, \end{aligned} \tag{A6}$$

and matrix elements at nuclear and magnetic reciprocal-lattice points,

$$\begin{aligned} &\langle e_+|j_+(1)\pm j_+(2)|g\rangle=\begin{bmatrix}0\\-\sqrt{2}\end{bmatrix}\equiv\beta_+\ , \\ &\langle e_-|j_-(1)\pm j_-(2)|g\rangle=\begin{bmatrix}0\\\sqrt{2}\end{bmatrix}\equiv\beta_-\ , \\ &\langle e_z|j_z(1)\pm j_z(2)|g\rangle=\begin{bmatrix}0\\1\end{bmatrix}=\beta_z\ . \end{aligned} \tag{A7}$$

The pair structure factor is

$$I_2(2J_{1/2})=(1-\hat{Q}_z^2)\beta_z^2+(1+\hat{Q}_z^2)(\beta_+^2+\beta_-^2)/4=\begin{bmatrix}0\\2\end{bmatrix}\ .$$

At a magnetic reciprocal-lattice point, the ratio of the structure factors of the triplet mode at $3J_{1/2}$ to the pair mode at $2J_{1/2}$ is therefore 32/9:2=16/9.

[1]See, e.g., J. Owen and E. A. Harris, in *Electron Paramagnetic Resonance,* edited by S. Geschwind (Plenum, New York, 1972), Chap. 6.

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