CRYSTAL-FIELD EFFECTS IN THE TWO-DIMENSIONAL ANTIFERROMAGNETS K_2FeF_4 AND $K_3Fe_2F_7$

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Mössbauer spectroscopy between 4.2 and 300 K combined with crystal-field calculations on Fe^{2+} have yielded information on the tetragonal crystal field and the spin–orbit coupling in the related structures K_2FeF_4 and $K_3Fe_2F_7$. Below T_N the electric-field gradient is asymmetric due to noncollinearity of the tetragonal and magnetic axes.

Mössbauer experiments and crystalline-field calculations are reported on the two-dimensional quadratic-layer antiferromagnets K_2FeF_4 [T_N = (62.7 ± 0.6)K] and $K_3Fe_2F_7$ ($T_N \approx 93$ K). K_2FeF_4 is a member of the well-known K_2NiF_4 family; $K_3Fe_2F_7$ has a magnetic double-layer structure isomorphous with $K_3Mn_2F_7$. In both structures Fe^{2+} is surrounded by an octahedron of F^- ions, slightly elongated along the tetragonal axis. From a recent neutron study of K_2FeF_4 [1] it appeared that below T_N the anisotropy forces the spins along the crystallographic [110] axis. From earlier Mössbauer experiments below T_N [2] the quadrupole coupling parameter eQV_{ZZ} was found to be positive, while the asymmetry parameter $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ is nonzero. On the other hand, with regard to the crystal structure neutron diffraction [1] did not detect any deviations from perfectly tetragonal symmetry in the entire temperature regime studied (4.2–300 K). The nonzero η is therefore a direct manifestation of the noncollinearity of the magnetic and tetragonal axes. More complete data on eQV_{ZZ} and η, including the temperature dependence, are presented here.

The Mössbauer spectra below T_N were analyzed by least-squares fitting with the hyperfine field H_{hf}, the quadrupole coupling constant eQV_{ZZ}, and the asymmetry parameter η as adjustable parameters; above T_N only eQV_{ZZ} is to be adjusted. In fig. 1 we display the results of eQV_{ZZ} in the temperature range 4.2–300 K. Below T_N, eQV_{ZZ} is virtually constant in K_2FeF_4, whereas it falls by ≈ 20% in $K_3Fe_2F_7$. At any temperature, eQV_{ZZ} is smaller in the double layer. At the lowest temperatures, η = 0.07 for K_2FeF_4, gradually falling to zero toward T_N (fig. 2). The asymmetry in $K_3Fe_2F_7$ starts off at a higher level, $\eta = 0.17$, and also vanishes at T_N.

The Hamiltonian of the Fe^{2+} ion ($L = 2$, $S = 2$) may be written as

$$\mathcal{H} = B_4^0(O_4^0 + 5O_4^4) + B_2^0O_2^0 + \lambda \boldsymbol{L}\cdot\boldsymbol{S} + g\mu_B \boldsymbol{H}_{ex}\cdot\boldsymbol{S}, \quad (1)$$

where the O's denote the standard crystal-field operators. The dominant term is the cubic crystal field; the second term, representing the tetragonal distortion, and the spin–orbit coupling ($\lambda_{free\ ion}$ = – 140 K) are of about equal importance.

We have ignored the fourth-order tetragonal field, whose effects are nearly indistinguishable from those of the second-order term. The exchange term of course disappears above the transition in zero field. Below T_N, we treat the exchange in a molecular-field scheme, i.e., we solve self-consistently eq. (1) and the relation $g\mu_B H_{ex} = -J\overline{\langle S_x\rangle}^T$, with J the exchange constant. Note

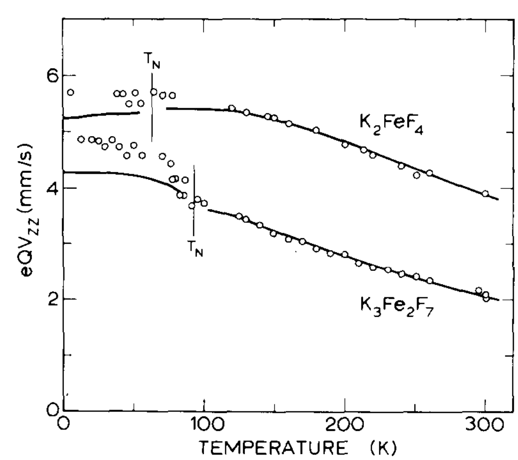

Fig. 1. The quadrupole interaction eQV_{ZZ} obtained from Mössbauer spectroscopy versus temperature. The solid lines represent the results of crystal field calculations.

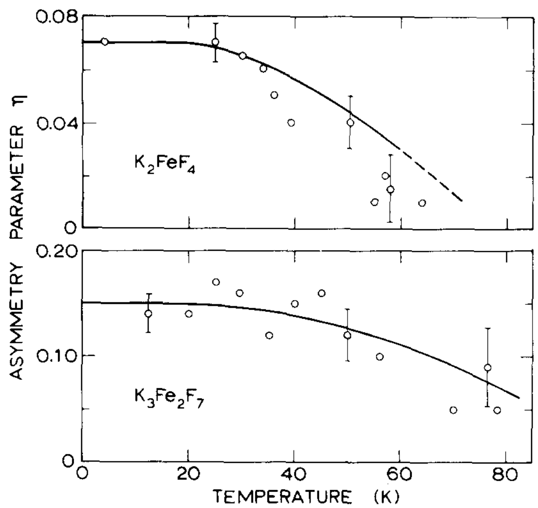

Fig. 2. The asymmetry parameter η versus temperature. The solid lines represent crystal field calculations including a molecular exchange field, but are scaled to the low-temperature data.

that the exchange-field is directed along the magnetic x-axis, which is the crystallographic [110] axis according to neutron diffraction [1].

The complete 25 × 25 Hamilton matrix was diagonalized numerically for various combinations of B_2^0, λ and J. The cubic splitting was set at 12000 K, noting that variation of B_4^0 only minutely affects the results. Additionally, expectation values of the quadrupole interaction and the spin were calculated. The temperature dependence of eQV_{ZZ} was subsequently evaluated by Boltzmann averaging.

In the paramagnetic regime, excellent fits to experiment could be obtained (solid curves in fig. 1) for $B_2^0 = (-60 \pm 5)$ K and (-20 ± 5) K in K_2FeF_4 and $K_3Fe_2F_7$, respectively; in both cases we find $\lambda = (-100 \pm 10)$ K. Below T_N, the fitting has been done with reference to supplementary results on H_{hf}, not detailed here, adopting the paramagnetic B_2^0 and λ. This yields $J = (-37 \pm 4)$ K and (-52 ± 6) K for K_2FeF_4 and $K_3Fe_2F_7$, respectively, the ratio of which reflects the difference in magnetic coordinations. All parameters being determined, it is now possible to calculate the electric-field gradients below T_N. Then, we indeed obtain an increment of eQV_{ZZ} for $K_3Fe_2F_7$, when going to lower T (solid curve in fig. 1). In addition, we find an exchange-field induced asymmetry η which is substantially larger for $K_3Fe_2F_7$ than for K_2FeF_4 (fig. 2). Thirdly, the calculated variation of η with temperature agrees well with experiment, although there remains a factor of about 3 in the absolute magnitudes.

In summary, the simple approach of eq. (1) produces excellent results for the field gradient above T_N. Below T_N the agreement between calculation and experiment is poor quantitatively, but at least the salient features are reproduced correctly. It is finally worth pointing out that the in-plane anisotropy parameter E in the spin Hamiltonian term $E(S_x^2 - S_y^2)$ as derived from neutron scattering [1], follows the same variation with temperature as η.

References

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[2] M. P. H. Thurlings, E. M. Hendriks and H. W. de Wijn, Solid State Commun. 27 (1978) 1289.