Magnetic Properties of the Planar Antiferromagnet Rb_2FeF_4

G. K. WERTHEIM, H. J. GUGGENHEIM, H. J. LEVINSTEIN, D. N. E. BUCHANAN, AND R. C. SHERWOOD
Bell Telephone Laboratories, Murray Hill, New Jersey

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Rb_2FeF_4, a K_2NiF_4-structure planar antiferromagnet with large anisotropy and spins perpendicular to the c axis, has a broad susceptibility maximum at 90°K. Mössbauer effect shows no long-range order in the interval 60–90°K. Between 50 and 60°K there is a gradual transition to long-range order accompanied by a crystallographic distortion. Three-dimensional order exists only at low temperature in the distorted crystal.

IT has recently been shown theoretically that the two-dimensional, isotropic Heisenberg model with finite-range interactions can be neither ferromagnetic nor antiferromagnetic at nonzero temperature.[1] This proof does not rule out infinite susceptibility in the limit of small external field and thus is not in contradiction with the conclusion of Stanley and Kaplan[2] based on spin-wave arguments. It is not known whether similar results obtain in the presence of anisotropy. We have experimentally investigated the nature of the magnetic order in a planar antiferromagnet with large anisotropy and find results very similar, except for a crystallographic distortion, to those reported in isostructural compounds with small anisotropy.

The investigation was conducted with the new compound Rb_2FeF_4, which was shown by powder and single-crystal x-ray crystallography to have the K_2NiF_4 structure with $a=4.176$ Å and $c=13.6$ Å. In this structure, perovskitelike layers containing a square planar net of Fe^{2+} ions are separated from each other by RbF layers. Symmetry arguments show that the magnetic interaction between adjacent layers vanishes.[3] The Rb_2FeF_4 was prepared from FeF_2 made by heating high-purity metallic iron in HF at about 900°C and from high-purity commercial RbF. Stoichiometric amounts were zone melted under an inert atmosphere. Spectroscopic analysis showed K in the range 0.1 to 0.5 wt% as the dominant impurity. The effect of K on the magnetic properties should be minimal, since the related compound K_2FeF_4, which also has the K_2NiF_4 structure, has similar magnetic properties.

The Mössbauer spectra were obtained with a conventional constant-acceleration spectrometer. The radioactive source consisted of ^{57}Co diffused into palladium. The samples were made either from cleaved single-crystal pieces or from powder crushed in dry nitrogen and cast with epoxy binder into thin slabs. For measurements at 4.2 and 20.4°K the samples were immersed in the cryogenic liquids. For other temperatures they were in the Dewar vacuum but connected to the liquid reservoir by a variable thermal resistance. The temperature was controlled by a differential thermocouple between the sample and the liquid-hydrogen reservoir, and a heater in the sample block.

The susceptibility of Rb_2FeF_4, Fig. 1, has the characteristics associated with such planar magnets,[4] i.e., it has a broad maximum and falls off slowly in the paramagnetic region. The data are similar to those reported for K_2CoF_4,[5] and, except for the effects of anisotropy, also to those of K_2MnF_4[6] and K_2NiF_4.[5] The susceptibility with the external magnetic field parallel to the c axis shows that the spin direction is perpendicular to the symmetry axis. This is different from the other case with large anisotropy, K_2CoF_4, where the spins are parallel to the c axis. The direction of the spins in the plane was ascertained from data with H along [100] and [110] directions. In neither case does χ approach zero at low temperature. This is in accord with the domain structure observed in optical-rotation studies, which show regions with deformation in mutually perpendicular directions below ~50°K. The lowest χ is obtained with H in a [100] direction. Under these circumstances, the spins in one half of the domains are parallel to H and the rest perpendicular. The susceptibility at $T=0$ then is $\frac{1}{2}\chi_\perp$ in the plane. The susceptibility with H along [110] should be $\sqrt{2}$ as large, as is indeed observed.

The Mössbauer-effect data confirm that the spins lie perpendicular to the c axis. Detailed analysis of the low-temperature spectra show an optimum fit when the magnetic field is taken along the minor axis of an almost axially symmetrical electric field gradient (EFG) tensor. The results rule out canting greater than a few degrees. The quadrupole splitting and isomer shift, Table I, are similar to those of FeF_2, another divalent iron fluoride, and are well behaved over the entire temperature range. At high temperature, powdered samples exhibit quadrupole splitting with a slight line-intensity asymmetry suggestive of Karyagin effect.[7] The asymmetry persisted even when the absorber was rotated by 45° with respect to the γ-ray direction, ruling

[1] N. D. Mermin and H. Wagner, Phys. Rev. Letters **17**, 1133 (1966).
[2] H. E. Stanley and T. A. Kaplan, Phys. Rev. Letters **17**, 913 (1966).
[3] M. E. Lines [Phys. Letters **24A**, 591 (1967)] has discussed the properties resulting from the two-dimensional character of this lattice.
[4] M. E. Lines, Phys. Rev. **164**, 736 (1967).
[5] K. G. Srivastava, Phys. Letters **4**, 55 (1963).
[6] D. J. Breed, Phys. Letters **23**, 181 (1966); Physica **37**, 35 (1967).
[7] V. S. Karyagin, Dokl. Akad. Nauk SSSR **148**, 1102 (1963) [English transl.: Proc. Acad. Sci. USSR, Phys. Chem. Sect. **148**, 110 (1964)].

out line-intensity asymmetry due to preferential orientation of crystallites in the absorber.

The Mössbauer spectra below the temperature of the susceptibility maximum, Fig. 2, provide additional information concerning the transition to the ordered state. From 60 to 90°K the spectra are indistinguishable from those at high temperature, indicating that there is no long-range order. Short-range order may be present, but the relaxation time of the spins must be very short, i.e., less than 10^{-11} sec, because the magnetic hfs interaction is completely averaged out.

The transition to the ordered state takes place between 50 and 60°K, as shown in Fig. 3. This is similar to the findings in K_2MnF_4, where significant anisotropy in the susceptibility, indicative of long-range order, appears only below $0.6T_{\chi_{max}}$.[6] All aspects of the observed behavior are compatible with an interpretation based on the assumption that there is a gradual increase in the

TABLE I. Parameters of hfs interaction at selected temperatures.

T (°K)	IS[a] (cm/sec)	QS[b] (cm/sec)	η[c]	H_{eff}[d] (kOe)
298	0.115_1[e]	0.204_1	...	...
195	0.121_1	0.245_1	...	...
78	0.126_1	0.280_1	...	...
20.4	0.127_2	0.280_2	0.049_5	355_2
4.2	0.127_2	0.277_2	0.065_5	364_2

[a] Isomer shift relative to the ^{57}Co in palladium source.
[b] Quadrupole splitting $\frac{1}{2}e^2qQ(1+\frac{1}{3}\eta^2)^{1/2}$.
[c] Asymmetry parameter.
[d] hfs effective magnetic field.
[e] Subscripts denote probable errors in last significant figure.

spin-correlation time of the short-range order. However, similar behavior would also be observed if the Néel transition were spread over a 5°K interval, leading to a superposition of paramagnetic and magnetically ordered hfs. Experiments with powdered material show that this transition is indeed structure sensitive, taking place over a wider range of temperature in material in which the two-dimensional nature has been at least partially destroyed by slip. This suggests that stacking faults could be responsible for the 5°K spread in the transition temperature.

It is unlikely that chemical impurities are responsible for the spread in the transition. Potassium, the major impurity, is present in from 0.6 to 3.0 mole % in our samples but their properties do not depend measurably on K content. K_2FeF_4 has similar magnetic properties and also exhibits a gradual transition to long-range order, but its transition temperature is higher by ~15%. As a result, the net broadening expected for our impurity content is only 0.3°K. It was ascertained that weak magnetic fields, ~200 Oe, do not affect the transition. In planar ferromagnets, weak magnetic fields

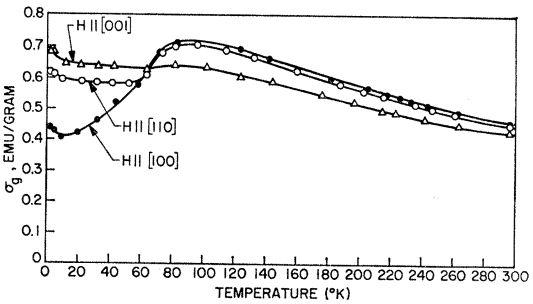

FIG. 1. Susceptibility of Rb_2FeF_4 in a field of 15 300 Oe.

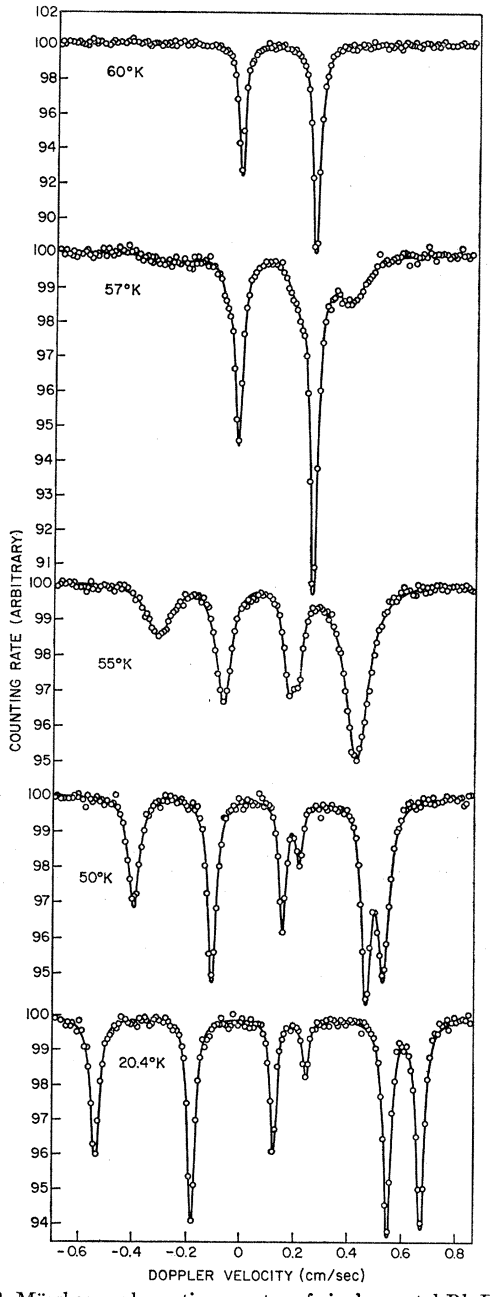

FIG. 2. Mössbauer absorption spectra of single-crystal Rb_2FeF_4 oriented with the c axis parallel to the direction of the γ rays.

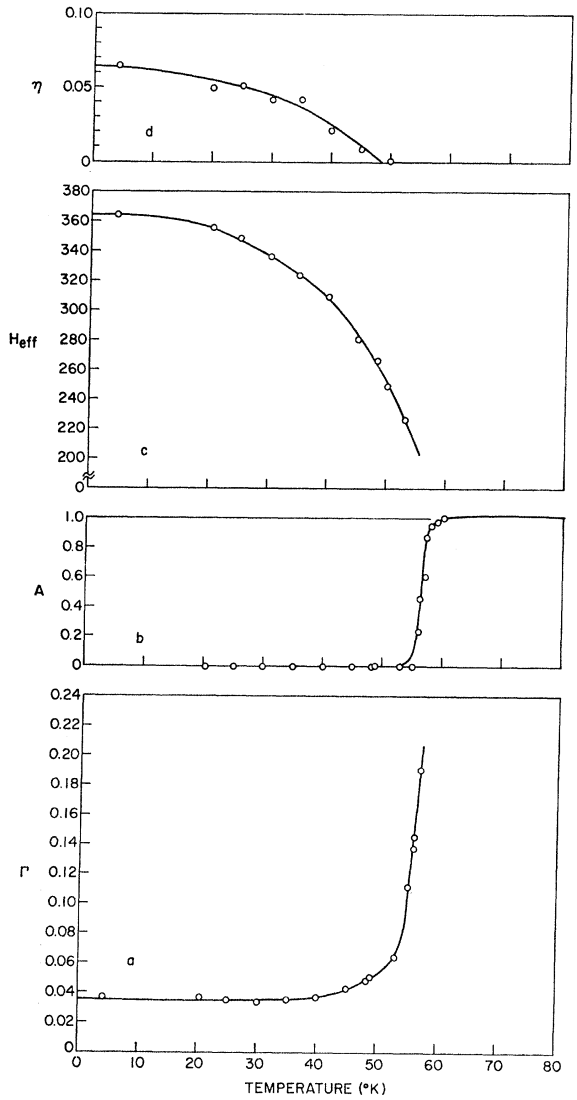

FIG. 3. Parameters of single-crystal absorption spectra. Γ is the linewidth in cm/sec of the lowest energy line as obtained from a least-squares fit; A the fraction of the area in the quadrupolar doublet; H_{eff} the hfs effective magnetic field in kOe, and η the asymmetry parameter of the EFG tensor. The quadrupole splitting is independent of temperature in this region, see Table I.

could induce long-range order; in planar antiferromagnets no effect is expected.

Below 45°K the linewidths of the Mössbauer spectra give no indication of relaxation broadening. This is indicative of long-range order, but is in principle also compatible with short-range order having a very long correlation time. The latter is an unlikely alternative since short-range order at low temperature is predicted only for isotropic, two-dimensional systems. Furthermore, if the magnetic hfs at low temperature were the result simply of a long spin relaxation time then the dominant effect of raising the temperature would be line broadening rather than the reduction in the hfs effective field which is in fact observed, Fig. 3(c). The observation of optical rotation gives direct confirmation that the crystal has three-dimensional long-range order in this temperature range.

Mössbauer-effect absorption spectra, as well as optical-rotation studies, show that the transition to long-range order is accompanied by a crystallographic distortion which lowers the symmetry of the crystal. The latter show optically active domains with mutually perpendicular distortions when viewed along the c axis below 50°K. Careful analysis of the low-temperature Mössbauer absorption spectra shows that the EFG tensor departs significantly from axial symmetry, indicating that the fourfold axis has been destroyed. The results, Fig. 3(d), show increasing asymmetry with increasing sublattice magnetization, suggesting that the distortion is of magnetostrictive origin. Since the spins are perpendicular to the c axis, the anisotropic magnetostriction is expected to have this effect.

The crystallographic distortion may destroy the condition for the cancellation of interplane interactions and would thus promote three-dimensional order, but is not itself responsible for the appearance of long-range order. This follows from the observation of a similar transition to long-range order in the isostructural compound K_2CoF_4, in which the spins lie along the c axis. The effect of anisotropy on the transition to long-range order also appears to be minor since in both K_2MnF_4 (very small anisotropy) and Rb_2FeF_4 (large anisotropy), long-range order appears near $0.6T_{\chi\max}$.

The susceptibility of Rb_2FeF_4 has the characteristic features of a planar antiferromagnet with a broad maximum near 90°K. Mössbauer-effect measurements show no long-range magnetic order down to 60°K, i.e., even well below the susceptibility maximum. Between 50 and 60°K there is a gradual transition to long-range order. The appearance of long-range order is accompanied by a crystallographic distortion probably of magnetostrictive origin.

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