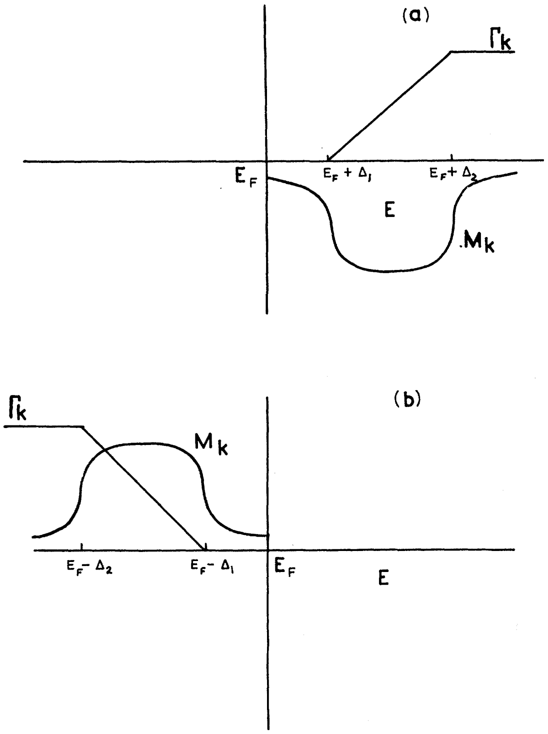

FIG. 1. The real and imaginary parts of the electron self-energy $\Sigma_k(E)=M_k(E)+i\Gamma_k(E)$. (a) Spin up; (b) spin down.

but there is some evidence for an anomalous bump at about 2°K.

Because of our assumption of noninteracting spin waves, our results are valid only for $T \ll J^2S/\epsilon_F$.

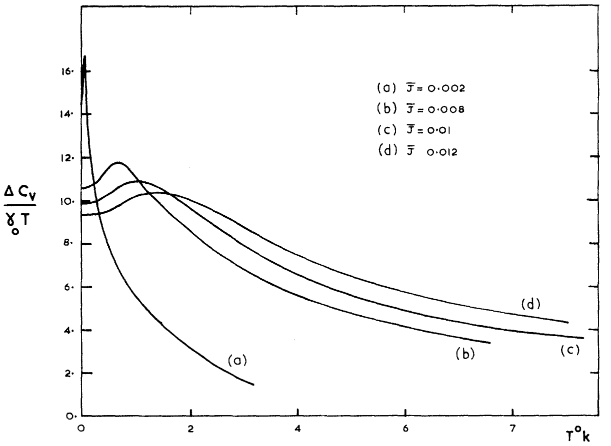

FIG. 2. Equation (5) as a function of T for various values of $\bar{J}=(JS/\epsilon_F)^2$.

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MAGNETIC AND STRUCTURAL TRANSFORMATIONS IN $RbFeF_3$

L. R. Testardi, H. J. Levinstein, and H. J. Guggenheim
Bell Telephone Laboratories, Murray Hill, New Jersey

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The perovskite compound $RbFeF_3$ has been found to exhibit ferromagnetic behavior at low temperature.[1,2] In this Letter we report the observations of (1) three crystallographic transformations each associated with distinct magnetic states, (2) sound velocity data which show the dominant effect of magnetic and structural reordering on the stability of the lattice, (3) distinct second- and first-order thermodynamic natures of the phase transformations (on cooling) to a metamagnetic and ferromagnetic state, respectively, and (4) an interaction between the magnetic and structural states strong enough to cause structural reorientation with small applied field. Beyond their intrinsic interest for $RbFeF_3$ we believe our findings may bear consequence on the behavior of a wide class of similar magnetic materials.

$RbFeF_3$ was synthesized by the reaction of molten RbF and FeF_2 in graphite or platinum crucibles under a purified He atmosphere. Single crystals, obtained by a horizontal-zone-pass method, generally showed low-angle boundaries with tilts of about 5°.

Magnetic behavior.– Three magnetic states have recently been identified in this compound.[1,2] It has been found[2] paramagnetic above 102°K, antiferromagnetic between 102 and 87°K, and ferromagnetic (i.e., exhibiting remanence) between 87 and 4.2°K with a modification of the magnetization behavior occurring at 45°K. We have made magnetization measurements[3] between 0 and 6 kOe on a long thin rod whose axis was within 10° of [110]. The temperature dependence of the magnetization σ in zero applied field is shown in Fig. 1. At 86°K the magnetization increases abruptly by 5 emu/g (which is 40% of the limiting value of this phase). Another transition occurs at 45°K but the data points are too coarsely spaced to establish a discontinuity in σ. At 4.2°K σ corresponds to 0.6 μ_B/molecule, which is in approximate agreement with the published value.[2]

Within 1° above the Curie point a large hysteretic magnetization could be induced in the material with applied fields of several thousand oersteds. The "transition" field for this metamagnetic behavior increased rapidly with increasing temperature. The transition field was about 4 kOe $\frac{1}{2}$° above the Curie point.

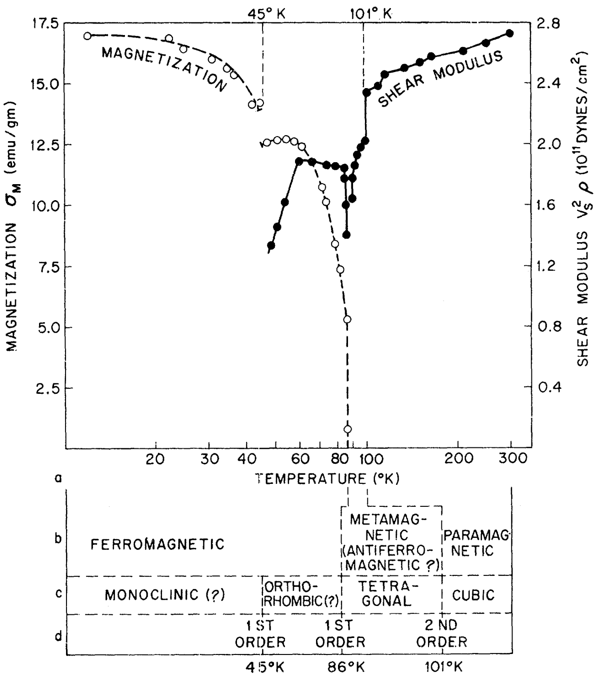

FIG. 1. (a) Magnetization and shear modulus, (b) magnetic state, (c) crystallographic state, and (d) transition order versus temperature. The two magnetization data points connected by the near vertical line "at" 86°K are separated by about 0.1°C. This is believed to be approximately the temperature and Curie-point uniformity through the sample. The microscopic studies at both Curie points show that the transformations (observed over a much smaller volume) occur in a visually instantaneous manner corresponding to a temperature interval probably smaller than 0.1°C.

Elastic behavior.—Pulse-echo measurements of the velocities of 20-Mc/sec shear and longitudinal sound waves were made in the temperature interval 300 to 4.2°K. The shear C_S and longitudinal C_L elastic moduli are obtained from the corresponding wave velocities v and the density[4] ρ using the relation

$$C = V^2\rho.$$

Over the temperature range of the measurements we have found $RbFeF_3$ to be elastically isotropic to within 5% for the velocities.[5] This surprising result allows the elastic behavior to be described by only one shear and one longitudinal modulus. The temperature dependence of the shear modulus, given in Fig. 1, shows a gradual (but anomalous) lattice softening between 300 and 100°K. At about 101°K the shear modulus falls by 15% in an apparently discontinuous manner. (A peak in the ultrasonic absorption is also observed.) On further cooling the modulus exhibits a continuous decline at increasing rate until at 86°K, with the shear modulus at near vertical slope, the attenuation becomes too large to detect echoes. At 85°K echoes are again detected and show the modulus to be rising on a near vertical slope. A further modulus decline occurs near 60°K and continues to 45°K below which the crystal is acoustically opaque.

X-ray structure.—Structural changes were determined from powder-pattern x-ray diffraction data. The first detectable change from the cubic (perovskite) structure was found at 97°K where a tetragonal distortion occurs with $c/a = 1.0012 \pm 0.0004$. The ratio c/a increases continuously to 1.0034 at 86°K. However, no change in the unit cell volume from the cubic phase value is found to within an uncertainty of 0.1%. At 86°K additional splittings of the diffraction peaks occur which show the symmetry to be less than tetragonal and probably orthorhombic.[6] At 45°K further abrupt changes in the diffraction pattern show another reduction in symmetry probably to a monoclinic class.

Microscopic structure.—Microscopic observations of single crystal slabs in crossed polarized light reveal structural domains in all magnetically ordered states. In the tetragonal and monoclinic phases the domains are defined by shear-type bands in (100) planes (referred to the cubic-state structure). In the orthorhombic phase the bands lie in (110) planes.[7] A strong magnetoelastic coupling in this crystal is evidenced by the fact that a rearrangement of the structural domain (and presumably crystallographic) orientation can be effected with the application of fields less than 250 Oe (which is roughly the saturation field) at temperatures near but below the Curie points.

The preceding results show an unusually strong relation between the magnetic, elastic, and structural behavior of $RbFeF_3$. The softening shear mode at high temperatures is both the precursor effect of a shear-type transformation at 101°K and the elastic "trigger" for the structural domains in the transformed state. This transition is thermodynamically of second order since no unit cell volume change occurs and all x-ray and microscopically observed distortions occur continuously on cooling. Such transformation will be accompanied by discontinuities in the elastic moduli. These discontinuities, which occur in a reversible process, may not be detected at an ultrasonic frequency unless the relaxation time τ for the new phase at or immediately below the transition is sufficiently short to follow the stress variations, i.e., $\omega\tau \ll 1$. Our results show that this condition is satisfied.[8]

The metamagnetic behavior above 86°K allows an estimate of the latent heat of the spontaneous magnetization. The Clausius-Clapeyron equation in magnetic variables is written[9] as

$$\frac{\Delta T}{\Delta H} = \frac{-T\Delta M}{Q_M}.$$

Close to 86°K the Curie point can be raised by about $\frac{1}{2}$°K with the application of 4 kOe. For $\Delta M = -5$ emu/g, $Q_M = 0.08$ cal/g (7×10^{-4} eV/molecule). It is not known whether those fields which induce the large moment also convert the crystalline structure to that found in the ferromagnetic phase.

The transition at 86°K to the ferromagnetic state is thermodynamically of first order. The identification is based on the spontaneous distortions found in both x ray and microscopic observations and the discontinuous change in magnetization at the Curie point. The softening of the shear mode in this case is so large and rapid as to admit near-zero restoring forces at the Curie point.[10] This behavior certainly facilitates the rearrangement of the shear bands at this temperature.[11]

The cooperative action leading to the transformation involves a balance of both magnetic and elastic energies. Bean and Rodbell[12] have shown that ferromagnetic transitions (which are second order in the molecular field theory) may become first order if the exchange energy is volume dependent. Such behavior is brought about by the "trading" of elastic energy for exchange energy in minimizing the free energy. Near the Curie point of $RbFeF_3$ the major coupling appears to be to shear (volume-conserving) deformations. Shear dependent exchange would also lead to first-order transformations in the above theory as well as an increase in compliance for shear deformations. Our results show that such magnetoelastic coupling, when large, may dominate the stability of the lattice near the transition point and thereby influence the transformation behavior. The crystallographic distortions of the ferromagnetic state are easily accomplished by shear transformations which lead to structural domains. The orientation of these domains may, throughout a given sample, alternate between several directions which were equivalent before transformation. The structural reorientation which we observed in a weak magnetic field may result because of a reduction in magnetic anisotropy energy for some structural domains.

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[3] Magnetization values were obtained by integrating the flux change through a coil whose core contained the sample. The M-H loops so obtained showed the remnant magnetization generally to be only about 5% (of the order of the experimental error) less than the saturation magnetization. In Fig. 1 we give remanence because of the complications of metamagnetism near the Curie point.

[4] The density is calculated to be 4.53 g/cc using the room-temperature x-ray lattice constant 4.513 Å (see Ref. 1). Thermal-contraction corrections have not been made for the low-temperature data.

[5] In view of the "polycrystalline" nature of the sample after a transformation, it is possible that some elastic anisotropy may escape detection.

[6] The distortion at 86°K is indicated by the increase in number of diffraction peaks associated with (310)

and (210) reflections above the number permissible for the tetragonal system. At 46°K there is a discontinuous change in the relative intensities of the peaks present and the introduction of further well-defined peaks. No attempt has been made to index the two lower symmetry structures since a unique set of indices cannot be obtained from the powder-pattern data alone.

[7] It is interesting that the magnetic domains, which have also been observed, change their direction at the monoclinic transition such that they cross the structural domains at 45° angles in both ferromagnetic phases.

[8] Using a simple relaxation model and the peak value of the observed attenuation we estimate that $\tau = 2\times 10^{-8}$ sec. The compressional modulus also exhibits a discontinuity at this transition from which a change of +10% in the adiabatic compressibility (on cooling) is calculated.

[9] A. J. P. Meyer and P. Taglang, J. Phys. Radium 14, 82 (1953).

[10] A similar behavior has been found in UO_2 [O. G. Brandt and C. T. Walker, Phys. Rev. Letters 18, 11 (1967)].

[11] Since the antiferromagnetic state is not a single structural domain, it may not be possible to see, at the Curie point, the elastic anisotropy which favors the new distortions of the ferromagnetic state.

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PHOTOCONDUCTIVITY IN ANTHRACENE CRYSTALS DUE TO EXCITATION OF TRIPLETS*

P. Holzman, R. Morris, and R. C. Jarnagin
Physics and Chemistry Departments, University of North Carolina, Chapel Hill, North Carolina

and

M. Silver
Army Research Office (Durham), Durham, North Carolina

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Two separate pulse-light sources, the first capable of producing singlets from which triplets are obtained by intersystem crossing, the second producing primarily a photon flux, have been used to produce a photocurrent in anthracene. An enhanced photocurrent is produced by the second flash well after the first flash has terminated. The decay of this effect appears to be characteristic of the lifetime of the triplets. The enhanced photoconductivity is believed to be a result of a tandem excitation process involving the triplets as the intermediate state.

Ever since the first demonstration of multiexcitation phenomena in molecular crystals giving rise to a photocurrent from intense pulse light sources,[1] which was attributed to an exciton-exciton interaction,[2] several other multiexciton and photon processes have been reported. Pope[3] observed a photoemission proportional to I^2; Hasegawa,[4] using a Q-spoiled laser, observed a photocurrent proportional to I^4; Kepler[5] and Courtens[6] also using a Q-spoiled laser observed a current proportional to I^3; and Kawada and Jarnagin observed a delayed photocurrent proportional to I^2 in high dielectric constant solvents using a xenon flash.

These various effects have been interpreted in terms of exciton-exciton interactions due to the one-photon population of singlets[1,3] and two-photon population of singlets,[4] although these interpretations have been criticized by Schott,[7] Kepler,[5] and Courtens.[6]

The I^3 dependence has been attributed to a two-photon production of singlets and their subsequent photoionization. Finally, the delayed ionization[8] in high dielectric constant solvents is attributed to triplet-triplet interactions.

To make a more complete picture of possible multiexcitation effects, we have searched for and found what we believe to be the first observation of a triplet photoionization. The two xenon flash lamps of 10^{-5}-sec duration used were triggered to be fired with a preset but variable interval between them. The radiation from the lamp triggered first was filtered with four Corning 3-73 filters plus a 450-mμ low-pass Optics Technology filter. These filters had less than 1% transmission at 4210 Å and below. The absorption coefficient for anthracene[9] at this wavelength is about 30 cm^{-1} and the average absorption coefficient for the light used was between 2 and 3 cm^{-1} depending on crystal thickness. In a 2-mm crystal the spatial dependence of the concentration