

for very helpful discussions.

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⁷This value should be compared with the value $k/B = 1.12 \times 10^5 \text{ m}^{-1} \text{ T}^{-1}$ calculated for a Fermi sphere with the same number of carriers per unit volume as copper.

⁸For k along [100] axis, no Gantmakher signal is detected because at the limiting point [100] the effective number of electrons is small. This is to be compared with the case of the alkali metals, where no Gantmakher waves are observed when k and B are perpendicular to the plate.

⁹It is well known that two waves can interact strongly when their phase velocities are equal or when one is strongly attenuated. Both interactions have been observed in the case of helicon-phonon coupling by C. C. Grimes (Ref. 4), and K. Saemark and P. K. Larsen, Phys. Letters **24A**, 668 (1967).

MAGNON ENHANCEMENT OF ELECTRONIC SPECIFIC HEAT

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Measurements of the electronic heat¹ of gadolinium indicate that the electronic density of states at the Fermi surface is a factor of the order of 8 times the free-electron value. Recent band-structure calculations by Dimmock and Freeman² show that the free-electron value is modified by a factor of 3. They suggest that the remaining discrepancy can be accounted for by electron-phonon enhancement.

In this paper we suggest that electron-magnon enhancement can also be of the same order of magnitude and could therefore be equally important in explaining the discrepancy.

We find also that for certain values of the coupling constant there is also a strong nonlinear dependence of the specific heat on temperature.

Gadolinium consists of ions of spin $\frac{7}{2}$ and a conduction band of three electrons per atom of a varied $s-d$ character.

The spin on the ions arises from the unfilled $4f$ shell. Neutron-diffraction experiments³ show that the $4f$ electrons are highly localized, the mean radius of the $4f$ shell being 0.35 \AA compared with the ion spacing of about 5 \AA . The interaction between the localized spins and the conduction electrons is taken to be the $s-f$ interaction

$$H_{sf} = -\frac{J}{N} \sum_{kk'} \exp[i(k-k') \cdot R_n] \{ S_n^Z [a_{k+}^\dagger a_{k'+} - a_{k-}^\dagger a_{k'-}] + S_n^+ a_{k-}^\dagger a_{k'+} + S_n^- a_{k+}^\dagger a_{k'-} \}, \quad (1)$$

where the a 's and a^\dagger 's are annihilation and creation operators for the conduction band and S_n^Z , S_n^+ , and S_n^- are the spin operators for the localized spin at the lattice site R_n .

As a consequence of this interaction three main effects arise:

(i) The conduction electrons are polarized. This effect is first order in J and since the measured magnetic moment per ion⁴ for gadolinium is greater than that of the free ion, we conclude that J is positive, i.e., a ferromagnetic interaction. The magnitude of J esti-

mated from these measurements is 0.08 eV , which agrees well with the value calculated for free electrons and localized $4f$ electrons.²

(ii) The polarization of the conduction electrons in turn leads to an effective coupling between the localized spins. This coupling is the well-known Ruderman-Kittel-Yosida (RKY) indirect exchange coupling which is second order in J . At low temperatures the normal modes of the localized spins due to this coupling are spin waves or magnons.

(iii) The RKY interaction does not account for the whole of the s - f interaction and as a consequence, one has scattering of conduction electrons by spin waves. This effect is also second order in J .

The electron-phonon enhancement arises from the creation and annihilation of virtual phonons; similarly, the electron-magnon enhancement arises from the creation and annihilation of virtual magnons. However, there are important differences between the two cases.

Firstly, because of the polarization of the conduction electrons, the Fermi surface for the spin-down electrons lies outside the Fermi surface for spin-up electrons. (Direction of quantization is in the $-z$ direction.) To create a spin wave at zero temperature, an electron on the spin-up Fermi surface has to be taken to the spin-down Fermi surface. Because of the gap between the Fermi surfaces, there will be a minimum energy for the creation of magnons by this process.

Secondly, because of the dispersion law for long-wavelength magnons and also the polarization effect, the lifetime of electrons in the neighborhood of the Fermi energy is significantly different from the lifetime because of the electron-phonon interaction.

We have calculated the electron self-energy part, using the perturbation theory developed by Giovannini, Peter, and Koide.⁵ The result

is, for an electron of energy E ,

$$\Sigma_k^\pm(E) = -\frac{2J^2 \langle S^z \rangle_0}{N} \sum_q \frac{f^\pm(\epsilon_{k-q} \mp \omega_q)}{E - \epsilon_{k-q} \mp \omega_q}, \quad (2)$$

where \pm indicate spin-up and spin-down electrons. f^+ is the Fermi function, $f^- = 1 - f^+$, and $\epsilon_k^\pm = \epsilon_k \pm JS$, where ϵ_k are the unperturbed single-electron energies. ω_q are the spin-wave energies arising from the RKY interaction. We have evaluated (1) using free-electron energies for the unperturbed states and a quadratic dispersion law with a cutoff ("Debye approximation") for the spin waves:

$$\begin{aligned} \omega_q &= cJ^2q^2, \quad q \leq q_{\max}; \\ c &= \frac{3}{8} \frac{J^2 S}{\epsilon_F k_F^2} q_{\max} \sim \frac{2\pi}{a}; \\ \omega_\epsilon &= 0, \quad q > q_{\max}; \end{aligned} \quad (3)$$

and a is of the order of the mean lattice spacing.

A schematic representation of the real and imaginary parts of the self-energy as functions of E , at $T = 0$, is shown in Fig. 1 for $k \sim k_F$. The fact that the imaginary part vanishes at $E = E_F \pm \Delta_1$, where $\Delta_1 = cJ^2(k_F - k_{F+})^2$, is a direct consequence of the polarization of the electron sea. As $J \rightarrow 0$, $\Delta_1 \rightarrow 0$, and it is this property which leads to the strong temperature dependence of the specific heat.

The entropy may be calculated from⁶

$$\Delta S^\pm = \frac{1}{T} \sum_k \int_{-\infty}^{\infty} d\epsilon \epsilon \frac{\partial f^\pm}{\partial \epsilon} \delta(\epsilon_k + \Sigma_k^\pm - \epsilon) \text{Re} \Sigma_k^\pm(\epsilon). \quad (4)$$

This gives a low-temperature contribution to the specific heat:

$$\frac{\Delta c_v}{\gamma_0 T} = \frac{9}{\pi^2} \int_{-\infty}^{\infty} dx n^2 \frac{\partial f^-}{\partial x} (kTx) \ln \left| \frac{\Delta_2/T + x}{\Delta_1/T + x} \right|, \quad (5)$$

where $\gamma_0 T$ is the unenhanced low-temperature specific heat, and Δ_2 arises from the maximum spin-wave energy and is given by $\Delta_2 = cJ^2 q_{\max}^2$. The normal low-temperature expansion of (5) gives

$$\lim_{T \rightarrow 0} \frac{\Delta c_v}{\gamma_0 T} = 3 \ln \left| \frac{\Delta_2}{\Delta_1} \right|, \quad (6)$$

which appears to diverge as $J \rightarrow 0$; however,

the radius of convergence of the expansion decreases with J . In Fig. 2 we plot Eq. (5) as a function of T for various values of $\bar{J} = (JS/\epsilon_F)^2$. The appropriate value for gadolinium is of the order of 0.01. For this case the specific heat is linear up to approximately 0.5°K. There is also a maximum at $T = 1.5^\circ\text{K}$. The experimental measurements are unreliable because of the presence of gadolinium oxide

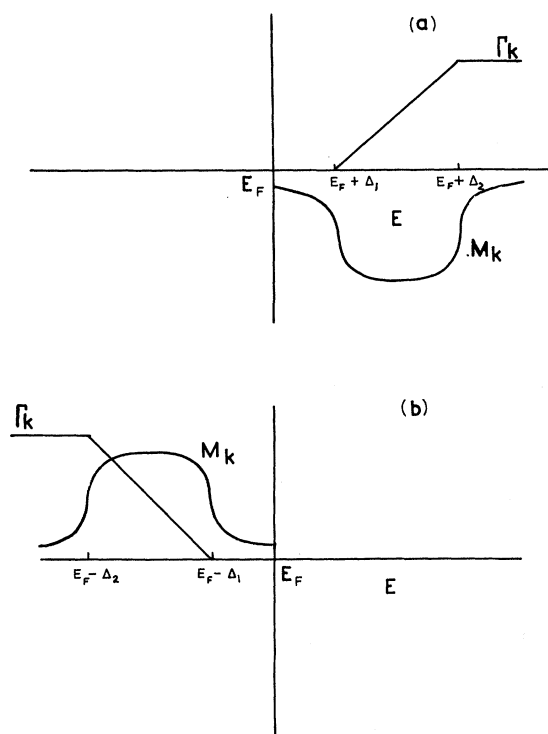


FIG. 1. The real and imaginary parts of the electron self-energy $\Sigma_k(E) = M_k(E) + i\Gamma_k(E)$. (a) Spin up; (b) spin down.

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

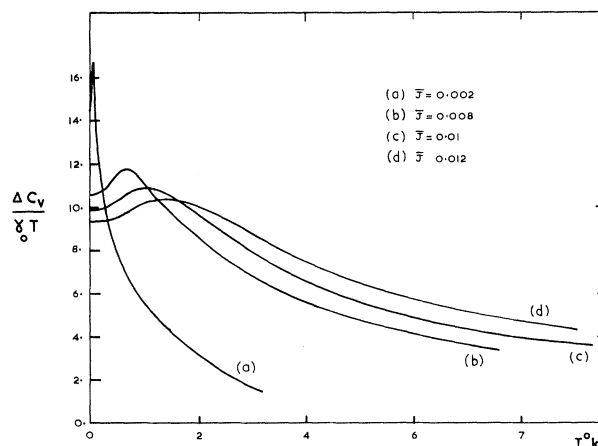


FIG. 2. Equation (5) as a function of T for various values of $\bar{J} = (JS/\epsilon_F)^2$.

$$\ll J^2 S / \epsilon_F.$$

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MAGNETIC AND STRUCTURAL TRANSFORMATIONS IN RbFeF₃

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The perovskite compound RbFeF₃ 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 RbFeF₃ we believe our findings may bear consequence on the behavior of a wide class of similar magnetic materials.

RbFeF₃ was synthesized by the reaction of molten RbF and FeF₂ 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 found² paramagnetic above 102°K, antiferromagnetic between 102 and 87°K, and