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Pressure Dependence of the Curie Temperature of Ferromagnetic Metals

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It is shown that according to the indirect exchange theory of ferromagnetic metals the pressure dependence of the Curie temperature is related to certain properties of the conduction electrons. A number of experiments are suggested to further our understanding of the problem.

In 1954, Patrick[1] reported the results of his measurements on the pressure dependence of the Curie temperature of several ferromagnets. These results have not been satisfactorily explained. The difficulty lies in the uncertainty of the conventional theory of ferromagnetism in making quantitative calculations since everything hinges on the size of the "exchange integral", a quantity so difficult to calculate that it is almost impossible to draw any dependable conclusion about its pressure dependence. Furthermore, many recent calculations all bear out the fact that the exchange integral is not enough to explain the ferromagnetism in transition elements.[2] In rare-earth metals the direct exchange should be extremely weak, because the magnetic $4f$ shells of different ions have little or no overlap. Hence, the magnetic interaction in these metals must come from an entirely different origin. It is generally believed that the indirect exchange mechanism via the conduction electrons is responsible for the magnetic interaction in these metals. The theory of indirect exchange as given by Ruderman and Kittel[3] and others[4–6] involves a set of parameters which characterize the properties of the conduction electron system and the strength of the electron-ion coupling. These parameters can be deduced from other experimental data. Therefore, it is possible to obtain a self-consistent theory of all the properties of the electron-ion system. This paper discusses the pressure dependence of the Curie temperature of gadolinium from the point of view of the indirect exchange theory. It shows that the pressure effect implies certain properties of the conduction electron wave function. Although the present knowledge of the electronic properties of the material is not sufficient to give a complete explanation, it is possible to assign reasonable upper and lower bounds to the relevant quantities.

In the indirect exchange theory, one assumes the total Hamiltonian of the electron-ion system to be

$$H=\sum_i \frac{p_i^2}{2m^*}+\sum_j I(\mathbf{r}_i-\mathbf{R}_j)\mathbf{s}_i\cdot\mathbf{S}_j, \tag{1}$$

where the first term is the kinetic energy of the conduction electrons in the effective mass approximation and the second term is the exchange interaction between the conduction electrons and the ions. $\mathbf{R}_j$, $\mathbf{S}_j$ are the position and spin of the jth ion, $\mathbf{r}_i,\mathbf{s}_i$ the position and spin of the ith electron, and $I(\mathbf{r}_i-\mathbf{R}_j)$ is the strength of the exchange interaction. The electron is described by a Bloch function $\phi_{\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$, where $u_{\mathbf{k}}(\mathbf{r})$ is periodic in the lattice. The Bloch function is normalized in a large volume V, the volume of the sample, so the matrix element of the exchange interaction can be written as

$$(1/N)\mathbf{s}_i\cdot\mathbf{S}_j I_{\mathbf{k}\mathbf{k}'}\exp[i(\mathbf{k}-\mathbf{k})\cdot\mathbf{R}_j], \tag{2}$$

where

$$I_{\mathbf{k}\mathbf{k}'}=N\int \phi_{\mathbf{k}'}^*(\mathbf{r})I(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r})d\mathbf{r}. \tag{3}$$

N is the total number of ions in V. In the second-order perturbation theory the interaction between the spins can be expressed by the spin Hamiltonian[3–5]

$$H_s=\sum_{i\neq j}\sum_j J(R_{ij})\mathbf{S}_i\cdot\mathbf{S}_j, \tag{4}$$

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with

$$J(R)=\frac{|I|^2}{4N^2}\frac{m^*V^2}{(2\pi)^3\hbar^2R^4}\times[2k_FR\cos(2k_FR)-\sin(2k_FR)], \quad (5)$$

where $|I|^2$ represents the average matrix element for $k, k'\cong k_F$; k_F is the Fermi momentum. It is more convenient to write $J(R)$ alternatively as

$$J(R)=(3\pi Z/4N)|I|^2N(\epsilon_F)F(2k_FR), \quad (6)$$

where Z is the valence of the ion, $N(\epsilon_F)$ the density of states at the Fermi level, and $F(x)$ is defined by

$$F(x)=(x\cos x-\sin x)/x^4. \quad (7)$$

In gadolinium, de Gennes[7] showed that this interaction makes a ferromagnetic state of the spins more stable than the random spin state. He also estimated that the value of $|I|$ which gives the correct Curie temperature would also give the correct anomalous resistivity. The actual ground state of the spins as the result of this interaction is not yet rigorously established.

If one assumes that the true ground state is ferromagnetic, one finds the energy of the state to be

$$E=\frac{3\pi Z}{4}|I|^2S^2N(\epsilon_F)\sum_j F(2k_FR_j), \quad (8)$$

where R_j is measured from the origin. To investigate the pressure effect, one needs to examine the volume dependence of the various factors in Eq. (8). For rare-earth metals, Z and S are volume independent. The summation is volume independent if the electron system is isotropic, because

$$k_FR_j\propto(k_F{}^3V)^{1/3}\propto(ZN)^{1/3}=\text{const.}$$

Anisotropy in the electron system will make the sum slightly volume dependent, but this effect will be ignored for lack of sufficient knowledge. Therefore, the following result is obtained

$$\partial\ln|E|/\partial\ln V=\partial\ln N(\epsilon_F)/\partial\ln V+\partial\ln|I|^2/\partial\ln V. \quad (9)$$

Since the Curie temperature is proportional to the ordering energy per spin, one also obtains

$$\partial\ln T_c/\partial\ln V=\partial\ln N(\epsilon_F)/\partial\ln V+\partial\ln|I|^2/\partial\ln V. \quad (10)$$

The quantities on the right-hand side of Eq. (10) are unknown. Therefore it is not possible to explain the pressure effect. However, using some simple arguments and the experimental value of $\partial\ln T_c/\partial\ln V$, one can put limits on the quantity $\partial\ln N(\epsilon_F)/\partial\ln V$. The $4f$ shell in rare-earth ions is highly stable, so the volume dependence of the matrix element is determined mainly by the variation of the Bloch function. This is closely analogous to the pressure dependence of the Knight shift in metals. It was found both theoretically[8] and experimentally[9] that the nuclear hyperfine interaction matrix element in alkali metals has the volume dependence $V^{-\eta}$, where $0<\eta<1$. Therefore, in the present problem it is reasonable to expect that

$$-1<\partial\ln|I|/\partial\ln V<0. \quad (11)$$

Physically the two limits represent two extreme considerations. If it is assumed that the amplitude of the Bloch function is uniformly scaled down when the volume expands, the matrix element would be inversely proportional to the volume. If the variation in volume affects only the part of the Bloch function near the boundary of the unit cell but not the part inside the ion, the matrix element would be independent of the volume. Actually, the Bloch function depends partly on the ionic potential, which is volume independent and partly on the boundary condition. Therefore, it varies in a way that is intermediate between the two extremities. The value of $\partial\ln T_c/\partial\ln V$ for Gd is calculated from Patrick's data,[1]

$$\partial T_c/\partial p=-1.2\times10^{-3}\ {}^\circ\text{K/atm},$$

the compressibility of gadolinium,[10] $K=(1/V)dV/dP=2.58\times10^{-6}\ \text{cm}^2/kg=2.66\times10^{-6}\ \text{atm}^{-1}$, and the Curie temperature,[10] $T_c=289\ {}^\circ\text{K}$. One finds

$$\partial\ln T_c/\partial\ln V=1.6. \quad (12)$$

If one combines this with Eq. (11), one obtains

$$1.6<\partial\ln N(\epsilon_F)/\partial\ln V<3.6.$$

Since the Sommerfeld constant γ involved in the electronic specific heat is proportional to $N(\epsilon_F)$, one also obtains

$$1.6<\partial\ln\gamma/\partial\ln V<3.6. \quad (13)$$

The quantity $\xi=\partial\ln\gamma/\partial\ln V$ has been directly measured for a number of materials.[11–14] The values reported are mostly in the range $0.5<\xi<4$. Hence, the limits in Eq. (13) are entirely reasonable.

It seems worthwhile at this point to propose some experiments that will give information about the size of ξ for gadolinium. The quantity ξ has been rather extensively studied for superconductors by relating it to the pressure dependence of the critical field.[11–13] Since hexagonal lanthanum is a superconductor and has lattice parameters very close to Gd, one may perform the experiment of reference 11 on La and from the

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result infer the property of Gd. For nonmagnetic, nonsuperconducting metals Andres[14] devised a method of measuring ξ by relating it to the low-temperature thermal expansion and specific heat. One may also learn about Gd by doing this experiment on lutetium, a rare earth which has the required qualifications. A direct measurement of ξ for Gd can be made by a slight variation of Andres' method. The specific heat of a ferromagnetic can be expressed by

$$C=\gamma T+f_1(T/T_c)+f_2(T/\theta_D), \tag{14}$$

where $f_1(T/T_c)$ is the spin-wave contribution, $f_2(T/\theta_D)$ is the phonon contribution, and θ_D is the Debye temperature. At low temperatures f_1 dominates f_2 because it has a temperature dependence like $T^{3/2}$. By a generalized Grüneisen relation[15] one finds that the low-temperature thermal expansion coefficient should have the temperature dependence

$$=AT+BT^{3/2}+\cdots, \tag{15}$$

where $A=K(\partial\gamma/\partial V)$ and K is the low-temperature compressibility.[14 16 17] Therefore, a careful measurement of the specific heat and the thermal expansion of Gd at low temperatures should enable one to determine both γ and $\partial\gamma/\partial V$. Hence,

$$\partial \ln\gamma/\partial \ln V=V\alpha_e/KC_e, \tag{16}$$

where α_e denotes the electronic contribution to the thermal expansion coefficient and C_e the electronic specific heat. The separation of the spin-wave term and the electronic term can be made easier if an external field of moderate strength is applied. In a field H, the spin-wave term is modified by an exponential factor[18] $\exp(-T/T_0)$, where $T_0=g\beta H/k$, g is the Landé factor, and β is the Bohr magneton. For Gd a field of 10 kG gives $T_0 \cong 1.5$°K. This should suppress the spin-wave term enough so that a reliable determination of the electronic term can be made. On the other hand, this field is too low to cause a change in electron energy levels and its associated effects.

Similar to the Knight shift in metals, the electron-ion exchange interaction also produces a shift in the paramagnetic resonance line of the Gd ion in metals. According to Yosida,[5] this shift is proportional to $N(\epsilon_F)$ and the diagonal matrix element of $I_{kk'}$. Jaccarino *et al.*[19] made use of this effect to determine the size and sign of I. The pressure dependence of this shift would give the value of $\partial \ln N(\epsilon_F)/\partial \ln V+\partial \ln|I|/\partial \ln V$. This together with Eq. (10) will enable one to find both ξ and $\partial \ln|I|/\partial \ln V$. In order not to disturb the conduction electron properties, one should do the experiment with either pure Gd or a solution of Gd in a hexagonal nonmagnetic rare earth.

Heavy rare-earth metals have the property that their paramagnetic Curie temperature is only a function of the number of electrons in the $4f$ shell.[7] This indicates that they have common electronic properties. Since $\partial \ln T_c/\partial \ln V$ is only a function of the electronic properties, it follows that $\partial \ln T_c/\partial \ln V=1.6$ for all rare-earth metals from gadolinium to thulium. This predicts the pressure dependence of the paramagnetic Curie temperature of these elements.

To conclude, it has been shown that in the light of the indirect exchange theory, the pressure dependence of the Curie temperature contains actually the information about the volume dependence of the Bloch function. The relationship given in Eq. (10) may be checked by independent experiments. It is very likely that the ferromagnetism in transition elements is also due to the indirect exchange mechanism. However, the present consideration of the pressure effect does not apply, because in these metals there is no clear distinction between the magnetic shell electrons and the conduction electrons. Hence, S is now a function of the pressure[20] and the electron-ion coupling is no longer well defined. The theory for these materials will involve more parameters.

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