Optics of Autoionizing Resonances in Nonlinear Spectroscopy, edited by N. Bloembergen (North-Holland, Amsterdam, 1977), and references therein [in particular, J. A. Armstrong and J. J. Wynne, Phys. Rev. Lett. 33, 1183 (1974)].

[9]A. Maruani, to be published.

[10]J. Ringeissen and S. Nikitine, J. Phys. (Paris), Colloq. 28, C3-48 (1969).

[11]K. Arya and A. R. Hassan, Solid State Commun. 21, 301 (1977).

[12]W. Ekardt and M. I. Sheboul, Phys. Status Solidi (b) 74, 523 (1976).

[13]E. Hanamura, Solid State Commun. 12, 951 (1973), and J. Phys. Soc. Jpn. 39, 1516 (1975).

[14]W. R. S. Garton, G. L. Grasdalen, W. H. Parkinson, and E. M. Reeves, J. Phys. B 2, 114 (1968).

Electromagnetic Effects near the Superconductor-to-Ferromagnet Transition

E. I. Blount and C. M. Varma
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 13 February 1979)

Electromagnetic effects are shown to govern the transition from superconductivity to ferromagnetism. A first-order transition to uniform ferromagnetism is predicted generally, but preceded by magnetic critical scattering which peaks at a finite wave vector.

Superconductors containing a periodic lattice of magnetic rare-earth ions have recently been discovered.[1,2] In some of them, as the temperature is decreased the superconducting state is followed by a transition to a ferromagnetic state[3] in which superconductivity disappears.

The theory of superconductors containing magnetic ions has been extensively studied,[4] particularly the effects of spin-flip scattering and conduction-electron polarization. Here we consider the effects of the interaction between the macroscopic magnetization $\vec{M}$, the electromagnetic field $\vec{A}$, and the superconducting order parameter $|\psi|$ and show that near the ferromagnetic transitions they play a dominant role in type-II superconductors.

We find that transitions from the superconducting state to two different states are possible as the temperature is decreased: a state of uniform magnetization which is not superconducting and a superconducting state in which the magnetization is oscillatory (spiral structure) at a wave vector of the order of $(\gamma\lambda)^{-1/2}$, where γ is the magnetic stiffness length and λ is the London penetration depth. For a reasonable choice of parameters, a first-order transition to the former is predicted, as is experimentally observed. This transition is, however, always preceded by a region of temperature in which $\chi(q)$, the wave-vector-dependent susceptibility, peaks at a finite wave vector, indicating a tendency toward the spiral state.

Our starting point is the free-energy functional:

$$F\{\psi,\vec{M},\vec{A}\}=\int d^3r\{\tfrac{1}{2}a|\psi|^2+\tfrac{1}{4}b|\psi|^4+p_0|(\nabla-ir_0\vec{A})\psi|^2 + (\vec{B}^2/8\pi)+\tfrac{1}{2}\alpha|\vec{M}|^2+\tfrac{1}{4}\beta|\vec{M}|^4+\tfrac{1}{2}\gamma^2|\nabla\vec{M}|^2-\vec{B}\cdot\vec{M}+\tfrac{1}{2}[\eta_1\vec{M}^2+\eta_2|\nabla\vec{M}|^2]|\psi|^2\}. \quad (1)$$

In Eq. (1) $\vec{B}=\nabla\times\vec{A}$. Also $a=a_0(T-T_c)/T_c$, where T_c is the upper superconducting transition temperature and $r_0=2e/\hbar c$. The London penetration depth $\lambda(T)$ is given by $\lambda^{-2}=4\pi p_0 r_0^2|\psi|^2$, $\alpha=\alpha_0(T-T_m')/T_m'$. The terms $\frac{1}{2}[\eta_1\vec{M}^2|\psi|^2+\eta_2|\nabla\vec{M}|^2]|\psi|^2$ express the effects of conduction-electron polarization and of spin-flip scattering on superconductivity.

The uniform superconducting state has the free-energy density

$$F_c=-a^2/4b \text{ for } T<T_c. \quad (2)$$

If $|\psi|\neq 0$, then $B=0$ in the bulk of the sample, and the question of magnetic order does not arise until $T<T_m'$. If, however, $|\psi|=0$, then $B=4\pi M$, and the free-energy density for the uniform magnetic state (with $H=0$) is

$$F_M=-(\alpha-4\pi)^2/4\beta,\quad T<T_m^0, \quad (3)$$

and

$$T_m^0=(1+4\pi/\alpha_0)T_m'. \quad (4)$$

The latter state is locally stable with respect to fluctuations in $|\psi|$ because A increases with the size of the system when B is uniform. For situations of present interest, viz., $T_m{}^0 \sim 1$ K, α_0 is of order unity, so that $T_m{}^0 \gg T_m{}'$.

We now consider states of uniform $|\psi|$ with variable $M(r)$ and $A(r)$. From Eq. (1) we find, for a given transverse component of M and B,

$$(\hat{\alpha} + \hat{\gamma}^2 q^2) M_q - B_q = h_q, \tag{5}$$

$$-M_q + (4\pi)^{-1}[(1 + q^2\lambda^2)/q^2\lambda^2] B_q = 0, \tag{6}$$

where $\hat{\alpha} = \alpha + \eta_1 |\psi|^2$, $\hat{\gamma}^2 = \gamma^2 + \eta_2 |\psi|^2$, and h_q is a test field coupling to M_q. From (5) and (6) the stiffness of transverse magnetization modes at q is given by

$$[\chi_{MM}(q)]^{-1} = \hat{\alpha} - 4\pi + \hat{\gamma}^2 q^2 + 4\pi/(1 + q^2\lambda^2). \tag{7}$$

The maximum of $\chi_{MM}(q)$ occurs at $q_0{}^2$, where

$$q_0{}^2 = (4\pi/\hat{\gamma}^2\lambda^2)^{1/2} - \lambda^{-2}, \tag{8}$$

and

$$\chi^{-1}(q_0) = \hat{\alpha} - 4\pi[1 - (1/4\pi)^{1/2}\hat{\gamma}/\lambda]. \tag{9}$$

As α decreases, $\chi^{-1}(q_0)$ vanishes at a temperature we shall call $T_s(|\psi|)$. This signals a possible transition to a state of uniform $|\psi|$ and oscillatory long-range magnetic order. $T_s(|\psi|)$ is given by

$$[T_m{}^0 - T_s(|\psi|)]/T_m{}^0 \approx 4\pi^{1/2}(\hat{\gamma}/\lambda)/(\alpha_0 + 4\pi). \tag{10}$$

The most stable configuration below T_s must be circularly polarized, as it keeps M^2 constant and therefore minimizes M^4. The free energy of this spiral state is

$$F_s(|\psi|) = -\chi^{-2}(q_0)/4\beta + \tfrac{1}{2}a|\psi|^2 + \tfrac{1}{4}b|\psi|^4. \tag{11}$$

The minimization of F_s with respect to $|\psi|$ is best done numerically, especially when the η's cannot be ignored. We shall comment on the η's later; for situations of present interest they serve only to renormalize the parameters in what are essentially electromagnetic effects. Ignoring them, we obtain an estimate of F_s by using the unperturbed value for $|\psi|$:

$$F_s = -\chi^{-2}(q_0)/4\beta - a^2/4b, \quad T < T_s. \tag{12}$$

The actual value of $|\psi|$ will be somewhat lower than the unperturbed value, and therefore (12) is a lower bound.

Now we compare the free-energy expressions (2), (3), and (12) for the three states. Since $a^2/4b$ is of order $k_B{}^2 T_c{}^2/E_f V$ as $T \to 0$, whereas $\alpha^2/4\beta$ is of order $k_B T_m{}^0/V$ as $T \to 0$ (V is the volume per atom), the uniform magnetic state is always favored over the superconducting state at some temperature below $T_m{}^0$. The uniform magnetic state is also favored over the state of spiral magnetism over the entire temperature range below $T_m{}^0$ if

$$\frac{(\alpha - 4\pi)^2}{4\beta}\left(\frac{T_s - T_m{}^0}{T_m{}^0}\right)^2 > \frac{a^2}{4b}. \tag{13}$$

If the inequality is not satisfied, the spiral state is favored in a small temperature region below T_s; at lower temperatures the uniform magnetic state is again favored. A schematic comparison of the free energies of the three states is given in Fig. 1.

To sum up, the mean-field results give a first-order transition from the superconducting state to the uniform magnetic state if the inequality (13) is satisfied. For smaller $|T_s - T_m{}^0|$, a second-order transition to the spiral state is indicated followed by a first-order transition to the uniform magnetic state. For a reasonable choice of parameters the temperature region in which the spiral state is favored is very small, if it exists at all.

There are two important physical aspects to the spiral state. First, the electromagnetic effects provide an effective self-interaction energy for magnetism at finite q. This energy, obtainable directly by eliminating B_q from Eqs. (5) and (6), is

$$[-2\pi + 2\pi/(1 + \lambda^2 q^2)] M_q{}^2. \tag{14}$$

This, together with $q^2\gamma^2 M_q{}^2$, the magnetic stiffness energy, leads to magnetization being favored at q of the order $(\gamma\lambda)^{-1/2}$. Second, A^2 is bounded in the spiral state (as opposed to the

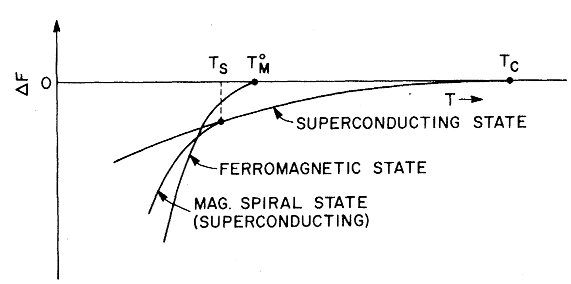

FIG. 1. Schematic variation of the difference in mean-field free energy between the normal state and the superconducting state, the ferromagnetic state, and the magnetic spiral superconducting state. The last is shown as stable in a small temperature interval in the figure, but would not be so for a smaller T_s.

state of uniform magnetization), so that superconductivity is preserved, though at a reduced value of $|\psi|$.

The situation we discuss is quite distinct from that considered by Anderson and Suhl.[5] They were interested in cases with strong exchange coupling between spins and conduction electrons, and especially in dilute spin systems. This leads to large values of the η's and of $\alpha_0/4\pi$. We are particularly concerned with cases where the exchange interaction is weak, as indicated by coexistence of superconductivity with concentrated local moments and by low Curie temperatures. This leads to small values of the η's and of $\alpha_0/4\pi$. The situation becomes particularly favorable when the superconductor has a very short coherence length, further reducing η_2. Our treatment is then valid when α and γ^2 arise from weak Ruderman-Kittel-Kasuya-Yosida interactions and/or local-field effects, the long-range dipolar interaction, of course, being described by the interaction with the magnetic field.

With (5) and (6) it is also possible to discuss, to a first approximation, the fluctuations about the mean-field result. First we note that χ_{BB}, which is measured by neutron diffraction, peaks at $q_B^2 = \hat{\alpha}/(\gamma^2\lambda^2 q_0^2)$, which can also be written

$$q_B^2 = q_0^2 + \frac{\hat{\alpha} - [(4\pi)^{1/2} - \hat{\gamma}/\lambda]^2}{\gamma^2\lambda^2 q_0^2}. \tag{15}$$

Thus above T_H, χ_{BB} peaks at a finite wave number which gradually deviates from q_0. The possible instability toward the spiral state can thus be observed experimentally by studying the q dependence of the critical scattering above the (first-order) transition.

The fluctuations make an interesting contribution to the free energy, which can be detected through a specific-heat experiment. We can calculate the contribution of the fluctuations to the free energy by a straightforward extension of the procedure of Halperin, Lubensky, and Ma[6] to include fluctuations of M as well as A. The result of this calculation is that the fluctuation contribution to the free-energy density relevant, say, to specific heat is

$$\Delta F_{\text{fl}} = \frac{k_B T}{6\pi^2}\left[\sum_i\left(-\tfrac{3}{2}q_c q_i^2\right) + \begin{cases} 2\pi\,\mathrm{Im}(q^3) \\ \pi\,\mathrm{Im}(q_1^3 + q_2^3)\end{cases}\right], \tag{16}$$

where the q_i's are the roots of $\chi^{-1}(q) = 0$ and where the first line applies when the roots are not pure real or imaginary, in which case q is the root in the first quadrant; the second line applies if the roots are pure imaginary and q_1 and q_2 are the roots on the positive imaginary axis. q_c is a cutoff wave vector of the order of the inverse zero temperature coherence length. Equation (16) is derived for $q_i > q_c$. For the general case a somewhat more complicated expression results.

In Fig. 2, ΔF_{fl} is plotted for $\gamma/\lambda = 10^{-2}$ and $q_c\lambda = 10$, and for $|\psi|$ at its unperturbed value. We have also plotted ΔF_{fl} for an ordinary ferromagnetic transition, i.e., $|\psi| = 0$, with the same approximations as above. The comparison of the two curves reveals the tendency of the superconductor to expel the magnetic fluctuations and of the latter to decrease $|\psi|$. A noteworthy feature of Fig. 2 is that a specific-heat bump is predicted to occur above T_m^0 (and therefore above the first-order transition temperature). With the specified parameter, the entropy density under this bump can be estimated from Fig. 2 to be about $10^{-1}k_B/\gamma^3$.

Turning now to real materials, first-order superconducting-to-ferromagnetic transitions have been observed in $HoMo_6Se_8$ (Ref. 7) and $ErRh_4B_4$.[3] A specific-heat bump of the kind described here

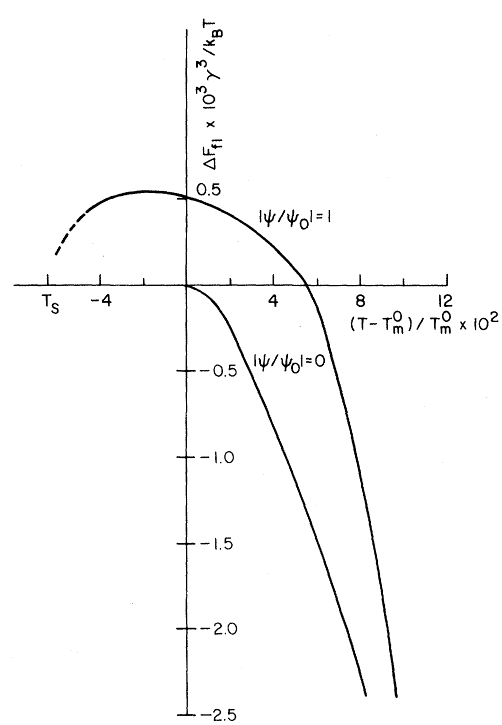

FIG. 2. The contribution to free-energy density of the fluctuations above T_s calculated from Eq. (16) for $|\psi|$ at its unperturbed value, $\gamma/\lambda = 10^{-2}$, and $q_c\lambda = 10$. Also shown is the free-energy density for $|\psi| = 0$. Our approximation for ΔF_{fl} is not good very close to T_s.

has been seen above the first-order transition in $ErRh_4B_4$.[8] In the same compound preliminary inelastic neutron scattering[9] has verified that $\chi_{BB}(q)$ peaks at a finite value of q as predicted here.

We were stimulated to undertake the present study through discussions with Dr. D. E. Moncton. We would also like to thank Professor B. I. Halperin and Professor M. B. Maple for discussions.

[1]O. Fischer, A. Treyvand, R. Chevrel, and M. Sergent, Solid State Commun. 17, 721 (1975); R. N. Shelton, R. W. McCallum, and H. Adrian, Phys. Lett. 56A, 213 (1976); W. A. Fertig, D. C. Johnson, L. E. DeLong, R. W. McCallum, M. B. Maple, and B. T. Matthias, Phys. Rev. Lett. 38, 987 (1977); M. Ishikawa and O. Fischer, Solid State Commun. 23, 37 (1977).

[2]B. T. Matthias, E. Corenzwit, J. M. Vandenberg, and H. E. Barz, Proc. Nat. Acad. Sci. USA 74, 1334 (1977); J. M. Vandenberg and B. T. Matthias, Proc. Nat. Acad. Sci. USA 74, 1336 (1977).

[3]D. E. Moncton, D. B. McWhan, J. Eckert, G. Shirane, and W. Thomlinson, Phys. Rev. Lett. 39, 1164 (1977).

[4]See, for instance, the review article by M. A. Jensen and H. Suhl, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic, New York, 1966), Vol. IIB.

[5]P. W. Anderson and H. Suhl, Phys. Rev. 116, 898 (1959).

[6]B. I. Halperin, T. C. Lubensky, and S.-k. Ma Phys. Rev. Lett. 32, 292 (1974).

[7]J. W. Lynn, D. E. Moncton, W. Thomlinson, G. Shirane, and R. N. Shelton, in Proceedings of the Twenty-Fourth Conference on Magnetism and Magnetic Materials, Cleveland, Ohio, November 1978 (J. Appl. Phys., to be published).

[8]M. B. Maple, J. Phys. (Paris), Colloq. 39, C6-1374 (1978), and private communication.

[9]D. E. Moncton, D. B. McWhan, G. Shirane, and W. Thomlinson, private communication; D. E. Moncton, in Proceedings of the Twenty-Fourth Conference on Magnetism and Magnetic Materials, Cleveland, Ohio, November 1978 (J. Appl. Phys., to be published).

Penning-Ionization Electron Spectroscopy of Chemisorbed CO

H. Conrad, G. Ertl, J. Küppers, and S. W. Wang
Institut für Physikalische Chemie, Universität München, München, Germany

and

K. Gérard and H. Haberland
Fakultät für Physik, Universität Freiburg, Freiburg im Breisgau, Germany
(Received 5 December 1978; revised manuscript received 26 February 1979)

Energy distributions of electrons ejected from clean and CO-covered Pd(111) surfaces by impact with metastable He* 2^1S (excitation energy $E^* = 20.6$ eV) and 2^3S ($E^* = 19.8$ eV) atoms were measured. The operation of the Penning mechanism, viz., $He^* + A \rightarrow He + A^+ + e^-$, is demonstrated for adsorbed CO whose valence orbitals could be identified. Thereby a new surface spectroscopic technique with extreme sensitivity to the outmost atomic layer is established.

Electron emission of metastable excited noble-gas atoms with clean and adsorbate-covered metal surfaces has been studied several times during recent years. The results, however, were often contradictory; the mechanism could not be established and almost no information on the surface properties could be obtanied.[1-6] If, on the other hand, gaseous atoms or molecules are used as targets, electron ejection takes place through the Penning ionization (= Auger de-excitation) process, viz.,

$$He^* + A \rightarrow He + A^+ + e^-, \qquad (1)$$

which has been well explored, both experimentally[7] and theoretically.[8] Similar conclusions were reached with condensed aromatics.[9,10] The kinetic energy of the emitted electrons, E_k, is then simply determined by the excitation energy of the metastable atom, E^* (= 20.6 eV in the case of 2^1S He), by the ionization energy of the target, E_i, and by the interaction potentials between the excited- and ground-state noble-gas atom with the target, $V^*(R)$ and $V(R)$, respectively. In the case of "hard core" interactions the variation with distance of the latter contributions becomes rather small so that E_i may be easily derived in a manner similar to ultraviolet photoelectron spectroscopy ($h\nu = 21.2$ eV for He I radiation). In

