RESISTIVE ANOMALIES AT MAGNETIC CRITICAL POINTS*

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By general arguments it is shown that the dominant contribution to the magnetic resistivity ρ_{mag} of a metal is due to the short-range spin fluctuations and hence that $d\rho_{mag}/dT$ should, in the static approximation, vary like the magnetic specific heat.

Recent experiments by Craig et al.[1] on the electrical resistivity of Ni near its Curie point have encouraged us to re-examine the theory of the resistive anomaly at the critical point of a metallic ferromagnet or antiferromagnet. We have concluded that existing theoretical treatments of this resistive anomaly, such as that of de Gennes and Friedel,[2] will often give qualitatively incorrect results. These treatments have predicted a singularity (cusp-like peak) in the resistivity supposedly arising from the long-range fluctuations of the magnetization near the critical point. In the following we argue that it is actually the short-range fluctuations which make the dominant contribution to the temperature-dependent part of the resistivity, so that one should see a very different kind of resistive anomaly.

Our arguments can be stated most clearly in terms of the model used by de Gennes and Friedel,[2] namely a lattice of magnetic ions with spins $\vec{S}_i$ at sites $\vec{R}_i$ and a single band of conduction electrons. This model seems to be rather unrealistic in the case of Ni; but our qualitative conclusions are more general. The interaction of a conduction electron with the array of spins will be described simply by

$$\mathcal{H}_{\text{electron ion}} = G\sum_i \delta(\vec{r}-\vec{R}_i)\vec{S}_i\cdot\vec{S}_e, \tag{1}$$

where $\vec{r}$ is the position of the electron and $\vec{S}_e$ its spin. We shall not worry about the fact that the magnetic electrons are not very well localized in many metals (e.g., Ni), and that they should then not be distinguished sharply from conduction electrons. Finally, in computing the scattering of a conduction electron from the magnetic system near its critical point, we shall assume that the spin fluctuations are so slow that we need not account for inelasticity. In other words, the amount of energy that an electron exchanges in a spin-flip scattering will be neglected so that all the relevant properties of the magnetic system may be described by an equal-time spin-spin correlation function. (Owing to the "thermodynamic slowing down" of critical fluctuations this is plausible for low wave numbers $\vec{k}$, but it may bear further investigation for the higher values of $\vec{k}$ which we claim are also important.)

The calculation of de Gennes and Friedel goes as follows. The resistivity due to spin scattering is

$$\rho = m/ne^2\tau, \tag{2}$$

where n, m, and τ are, respectively, the density of conduction electrons, their effective mass at the Fermi surface, and the relaxation time associated with scattering from spin fluctuations. If τ_0 is the relaxation time at temperatures so high that the spin-spin correlations are negligible, we have

$$\frac{\tau_0}{\tau} = \left(\frac{2\pi}{\sigma_0}\right)\int_0^\pi \sigma(\theta)(1-\cos\theta)\sin\theta d\theta, \tag{3}$$

$$\sigma_0 = (4\pi)^{-1}(mG/\hbar^2)^2 S(S+1), \tag{4}$$

where $\sigma(\theta)$ is the differential scattering cross section per magnetic spin, and θ is the scattering angle. If we use first-order Born approximation, sum over all final states, and perform a thermodynamic average over the initial states, we obtain the familiar formula,

$$\sigma(\theta) = (\sigma_0/4\pi)\sum_i \Gamma(\vec{R}_i)\exp(i\vec{K}\cdot\vec{R}_i). \tag{5}$$

Here $\hbar\vec{K}$ is the momentum transfer and

$$\Gamma(\vec{R}_i, T) = [\langle\vec{S}_i\cdot\vec{S}_0\rangle - \langle\vec{S}_i\rangle\cdot\langle\vec{S}_0\rangle]/S(S+1) \tag{6}$$

is the static spin-spin correlation function for two spins separated by a distance $\vec{R}_i$.

De Gennes and Friedel complete their calculation by evaluating $\Gamma(\vec{R}, T)$ in what amounts to the Ornstein-Zernike approximation.[3] By

tacitly assuming the approximation is valid for all R and T independently, one finds that τ/τ_0, and hence ρ, has a singularity of the form[1]

$$\rho(T) \approx \rho_c - b|t| \ln|t|^{-1}, \quad t = (T/T_c) - 1, \tag{7}$$

with $b > 0$, which means that the resistivity should have a finite, upward pointing cusp at T_c. Qualitatively similar results can be derived using modern extensions of the Ornstein-Zernike formula for the long-range part of the correlations[3] and by again assuming uniform validity in R and T.[4] The finite maximum at T_c predicted by all such treatments is in striking disagreement with the experimental results[1] for Ni which exhibit a monotonic increase of ρ with T through T_c, while $d\rho/dT$ has a sharp peak at T_c.

As our first point of criticism of the above theory, we observe that the sum in (5) cannot realistically be allowed to extend undamped to pairs of spins with indefinitely large separations $\vec{R}_i$ as is, in principle, supposed in the derivation of (7). The contribution to (5) from a single term in the sum represents the interference in the scattering of an electron wave incident upon two spins separated by $\vec{R}_i$. Even if these spins are strongly correlated, however, they will not scatter coherently if $\vec{R}_i$ is appreciably greater than the electron mean free path l. Since l remains finite through the Curie point,[5] we conclude that it is unphysical to suppose that the detailed form of the resistance anomaly is determined solely by the long-range part of $\Gamma(\vec{R})$. Rather, $\Gamma(\vec{R})$ should be damped by some factor, say $p(\vec{R})$, which decreases monotonically from unity on a scale fixed by l.[6]

Next, and more generally, insert (5) into (3) and integrate over the scattering angle θ. The resulting lattice sum is convergent, so that ρ remains finite at T_c, even without a damping factor. It again follows that the behavior of $\rho(T)$ cannot depend on the long-range part of $\Gamma(\vec{R})$ alone. To see this more explicitly, we average over orientations of the momentum transfer $\vec{K}$ relative to the crystal axes and assume a spherical Fermi surface of radius k_F so that $2\pi(1-\cos\theta)\sin\theta d\theta = \pi k_F^{-4} K^3 dK$. If R_s is the radius of the sth shell of spins surrounding the site $\vec{R}_i = 0$ and ν_s is the number of spins in that shell, we thus find that

$$\frac{\tau_0}{\tau} = \sum_{s=0}^{\infty} \nu_s f(R_s) p(R_s) \Gamma(R_s), \tag{8}$$

where $f(R)$ is the decaying oscillatory function

$$f(R) = \int_0^{2k_F} \frac{\sin KR}{R} \frac{K^2 dK}{4k_F^4} = \frac{1}{4k_F^4 R} \frac{d^2}{dR^2} \left(\frac{\cos 2k_F R - 1}{R} \right). \tag{9}$$

Since $f(0) = 1$, the term for $R_S = 0$ in (8) (the incoherent scattering) yields

$$(\tau_0/\tau)_{R_S = 0} = \Gamma(0) = 1 - |\langle \vec{S} \rangle|^2 / S(S+1). \tag{10}$$

This makes no contribution to $d\rho/dT$ above T_c, but below T_c the decrease of the resistivity will be proportional to $[M_0(T)]^2$, the square of the spontaneous magnetization. Most probably this will determine the dominant singularity in $d\rho/dT$ below T_c as $|t|^{2\beta-1}$.[3]

For $T > T_c$, on the other hand, $d\rho/dT$ must be wholly determined by the short-range correlations, in particular, by the temperature dependence of $\Gamma(R_S, T)$ for $R_S \neq 0$. For any fixed R_S we now argue quite generally that $\Gamma(R_S, T)$ must have the same dominant singularity at T_c as does the magnetic energy[7,8] which is given (for $T > T_c$) by

$$U(T) = -\sum_j J(R_j) \langle \vec{S}_0 \cdot \vec{S}_j \rangle = -\sum_{s=1} \nu_s J(R_s) \Gamma(R_s, T), \tag{11}$$

where $J(R)$ is the usual Heisenberg exchange energy. The relations (8) and (11) are obviously very similar in that both are convergent sums of terms containing the same temperature-dependent factors $\Gamma(R_S, T)$. We conclude, therefore, that $\rho(T)$ and $U(T)$ should have the same kind of singularity above T_c, and hence that $d\rho/dT$ should vary as $|t|^{-\alpha}$, that is like the magnetic specific heat.[3,9] The experiments on Ni seem consistent with this conclusion.[10]

A more detailed picture of the anomaly can be obtained by reformulating (8)-(10) as

$$\frac{\tau_0}{\tau} = \Gamma(0, T) + (8k_F^4)^{-1} \int_0^{2k_F} \hat{\Gamma}(K, T) K^3 dK, \tag{12}$$

$$\hat{\Gamma}(K, T) = \sum_{\vec{R}_i \neq 0} \Gamma(\vec{R}_i, T) p(\vec{R}_i) \exp(i\vec{K} \cdot \vec{R}_i). \tag{13}$$

Even at T_c the factor K^3 in (12) will overwhelm the singularity[3,11] $\hat{\Gamma}(\vec{K}, T_c) \sim 1/K^{2-\eta}$; evidently the resistive anomaly will be determined mainly by the temperature dependence of $\hat{\Gamma}(\vec{K}, T)$

for values of K near $2k_F$. We believe that this conclusion will pertain also to itinerant-electron models of ferromagnets with $\hat{\Gamma}$ being simply the Fourier transform of the spin-density correlation function.

The function $\hat{\Gamma}(\vec{K}, T)$ with $p \equiv 1$ has recently been studied extensively for the Ising model[12]; there is also relevant evidence from neutron scattering experiments, specifically on iron.[13] The qualitative behavior of $\hat{\Gamma}(\vec{K}, T)$ implied by these studies is shown in Fig. 1. At fixed K the transform $\hat{\Gamma}$ displays a rounded maximum above T_C located by $\kappa(T_{max}) \simeq K$, where the inverse range of correlation $\kappa(T)$ vanishes as $|t|^{\nu}$. This maximum is sharper and more pronounced for the lower values of K. At T_C a singularity of the form $|t|^{1-\alpha}\,\mathrm{sgn}\{t\}$ occurs.[14]

The sign of this singularity, and hence, on performing the integration in (12), the sign of the anomaly proportional to $|t|^{-\alpha}$ in $d\rho/dT$, can be confirmed by computing the transform (13) on the basis of the scaling hypothesis[3,8,15]

$$\Gamma(R, T) \approx D(\kappa R)/R^{1+\eta} \quad (R \neq 0). \tag{14}$$

The long-range (Ornstein-Zernike-like) decay is ensured by (i) $D(x) \sim x^{\eta} e^{-x}$ as $x \to \infty$; but to reproduce the (positive) specific-heat anomaly via (11) one must have (ii) $D(x) = D_0 - D_1 x^{(1-\alpha)/\nu} \times \mathrm{sgn}\{t\} - D_2 x^{1/\nu} + \cdots$ as $x \to 0$ with $D_1 > 0$.[8,14] If (ii) is inserted into (13) and the Fourier sum is approximated by an integral, one obtains from (12) an explicit expansion for τ_0/τ in which the coefficient of the term $|t|^{1-\alpha}\,\mathrm{sgn}\{t\}$ is positive provided (a) that $k_F l$ is sufficiently large,[16] and (b) that $(1+\eta)^{-1} > \nu/(1-\alpha) > (3+\eta)^{-1}$. [Condition (b) is satisfied by typical experimental and theoretical exponent values.[3]]

This expansion is valid only for $\kappa(T)/k_F \lesssim 1$. For large values of $|t|$ (and κ), or smaller values of k_F, one finds, as in Fig. 1, a more or less rounded peak in the magnetic resistivity above T_C. To compare with experimentally observed resistivities one must finally add a smoothly increasing contribution due to lattice scattering. For large k_F the rounded peak above T_C will then disappear into the lattice background, which apparently is what happens in Ni. For smaller k_F, however, the peak will appear as an anomaly reminiscent of, but analytically quite different from, that predicted by de Gennes and Friedel.

The theory outlined here should be applicable to a wide variety of resistive anomalies which are known to occur in the rare-earth metals.[17,18] We would like to encourage more accurate measurements of these anomalies with, if possible, accurate neutron-scattering and specific-heat studies of the same samples.

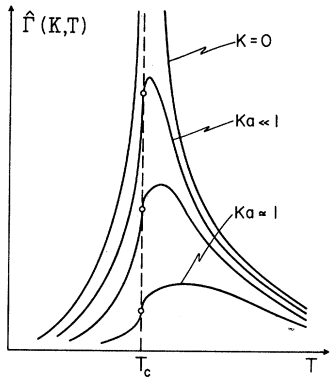

FIG. 1. Qualitative behavior of $\hat{\Gamma}(\vec{K},T)$ for various values of K relative to the lattice spacing a. For $K=0$, the curve represents the reduced differential susceptibility with its characteristic divergence at T_C.

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[1]P. P. Craig, W. I. Goldburg, T. A. Kitchens, and J. I. Budnick, Phys. Rev. Letters 19, 1334 (1967). See also Ya. A. Kraftmakher, Fiz. Tverd. Tela 9, 1529 (1962) [translation: Soviet Phys.—Solid State 9, 1199 (1967)]; W. Gerlach, Physik Z. 33, 953 (1932).

[2]P. G. de Gennes and J. Friedel, J. Phys. Chem. Solids 4, 71 (1958).

[3]See, for example, M. E. Fisher, J. Math. Phys. 5, 944 (1964), where the relevant critical exponents are defined.

[4]For $\eta > 0$ one finds that the singular term in Eq. (7) is replaced by $-b_1|t|^{2\nu} - b_2|t|^{(2+\eta)\nu}$ with $b_1, b_2 > 0$.

[5]For nickel l becomes comparable with the spin-spin correlation length $\xi = [\kappa(T)]^{-1}$ at temperatures within, probably, about 5 to 10 deg of T_C.

[6]In a more complete version of the theory of resistivity, including multiple scattering of the conduction electrons, it transpires that $\Gamma(R)$ should be modified by the factor $p(\vec{R}) = \exp(-R/l)$.

[7]See M. E. Fisher, Phil. Mag. 7, 1731 (1962).

[8]This is known to correct for two-dimensional Ising models; see, e.g., M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967).

[9]V. L. Pokrovskii has independently advanced this conclusion at the Seminar on Phase Transformations, Budapest, Hungary, 10-13 October 1967 (unpublished).

[10]Precise measurements of the specific-heat anomaly of nickel have been made by P. Handler, D. E. Ma-

pother, and M. Rayl, Phys. Rev. Letters 19, 357 (1967).
[11]We consider here the worst case: $p \equiv 1$. The exponent η is expected to be small; see Refs. 3 and 8, and M. E. Fisher and R. J. Burford, Phys. Rev. 156, 583 (1967).
[12]Fisher and Burford, Ref. 11.
[13]D. Bally, B. Grabcev, A. M. Lungu, M. Popovici, and M. Totia, J. Phys. Chem. Solids 28, 1947 (1967).
[14]This singularity is not specifically shown in Figs. 10 and 12 of Ref. 11 but its presence follows from the considerations presented here.
[15]M. E. Fisher, in Critical Phenomena, Proceedings of a Conference, Washington, D. C., 1965, edited by M. S. Green and J. V. Sengers, National Bureau of Standards Miscellaneous Publication No. 273 (U. S. Government Printing Office, Washington, D. C., 1966), pp. 108-115, especially Eqs. (40)-(45).
[16]For small $k_F l$ the opposite sign for the resistive anomaly cannot be excluded. It is also possible that the approximation of the sum in (13) by an integral might be misleading in this and certain other circumstances.
[17]B. R. Coles, Advan. Phys. 7, 40 (1958).
[18]R. V. Colvin, S. Levgold, and F. H. Spedding, Phys. Rev. 120, 741 (1960); H. E. Nigh, S. Levgold, and F. H. Spedding, Phys. Rev. 132, 1092 (1963).

SECOND-HARMONIC GENERATION OF LIGHT AT THE BOUNDARY OF ALKALI HALIDES AND GLASSES

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This Letter reports measurements of second-harmonic generation of light at the boundary of alkali halides and glasses along with further measurements of some semiconductors and metals. The second-harmonic power reflected from the surface of transparent materials was found to be lower by several orders of magnitude than that generated at semiconductor and metallic surfaces.[1-4] Second-harmonic generation was also studied in transmission through thin platelets of glass and LiF.

The second-harmonic generation in media with inversion symmetry has been discussed by several authors.[5-10] For centrosymmetric isotropic medium, the lowest order contribution to the nonlinear polarization at the second-harmonic frequency 2ω, denoted by $P_i(2\omega)$, may be given phenomenologically as

$$P_i(2\omega) = (\alpha-\beta)E_j(\omega)\nabla_j E_i(\omega) + \beta E_i(\omega)\nabla_j E_j(\omega) + \gamma\nabla_i[E_j(\omega)E_j(\omega)]. \quad (1)$$

The coefficients are expected to be of the order of 10^{-17} esu for transparent materials,[5] about 10^{-15} esu in semiconductors, and 10^{-14} esu in metals.[9] All materials will be assumed to be isotropic, as no signals due to the additional terms present with cubic crystals have been observed in this or previous experiments.[1]

For a transverse electromagnetic wave, the first two terms in Eq. (1) are zero in the bulk; the last term gives rise to a longitudinal polarization, and so it is observable only in experiments involving a discontinuity, such as the boundary of a medium. This bulk term alone cannot explain the observed effects, and a proper account must include phenomena associated with the surface itself. To this end, the model of Bloembergen[2,10] will be used. According to this model, the nonlinear surface effects arise primarily from the rapid variation of the normal component of the electric field over a thin layer at the boundary of the medium. Assuming that the thin layer has the same dielectric constant as that of the bulk, this model predicts that the surface effects can be described in terms of a nonlinear polarization equivalent to the α and β terms in Eq. (1). For layers thin compared with a wavelength, the corresponding second-harmonic amplitude depends on the total change of the normal component across the layer and is independent of the detailed variation within the layer.

An alternative model to describe the surface effects is to assume that the surface is piezoelectric.[1] General symmetry considerations show that the only new term distinguishable from the previous model is of the form $P_{\text{normal}}(2\omega) \propto E_j E_j$. A slightly different angular dependence not detectable in this experiment would follow from a term of this form.

The coefficients α, β, and γ are generally complex, but are real in a lossless medium. These coefficients can be determined by measuring the power and polarization of the second harmonic produced with the fundamental beam polarized at 45° and 90° with respect to the plane of incidence. Using Eq. (1) and as-