Heavy-hole excitonic effects in rare-earth compounds

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In order to explain some recent experiments on a variety of rare-earth compounds such as SmB_6 and the high-pressure phase of SmS, we propose a model consisting of conducting d and f electrons, the latter assumed to be infinitely heavy. They interact with each other by both non-spin-flip (V_0) and spin-flip (V_s) electron-electron interactions. We find that as far as the first-order renormalization-group method is concerned this system is equivalent to a one-dimensional (1-D) system that has become quite popular recently (the Menyhard-Solyom model). The correspondence has $V_0 = g_2 - g_1/2$ and $V_s = -2g_1$ in the usual notation. Owing to this interaction the system may or may not go through an "excitonic" phase transition. From the 1-D work of Solyom on the density-density response function, we conclude that V_0 will never cause a phase transition at any finite temperature, that only V_s may cause a phase transition, and that the temperature at which this occurs is unaffected by V_0. We argue that because V_s is much smaller than V_0, it is not important for the system and the range of temperature that is of interest. Neglecting V_s, we find that the conductivity is given by a formula $\sigma = Ne^2\tau/m$, where τ is given approximately by the equation $\tau^{-1} = \tau_0^{-1}[(T+\beta\tau^{-1})/E_F]^{-a}$, β here is a constant of the order of unity. We also discuss the resistivities of SmB_6, "metallic" SmS, TmS, and TmSe and find good agreement with the experimental results.

I. INTRODUCTION

In this paper we propose an explanation for a series of physical phenomena observed in a wide variety of materials such as SmB_6,[1] the high-pressure phases of SmS, SmTe, and SmSe.[2-4] In these substances, the Sm ion exists partly in a 3^+ state with an angular momentum $j = \frac{5}{2}$, while no Curie type of behavior is seen at low temperatures. The valences of Sm in these compounds are 2.8, 2.66, and 2.76,[2] respectively. Except for a coincidence in the band structure these compounds should be metal because there are more than two electrons per site coming from the samarium and yet the resistivity rises sharply by one or two decades as the temperature is lowered. There is another strange feature; these compounds all have an extremely large coefficient for the linearly temperature-dependent part of the specific heat—about 100 times that of copper. In this paper, we shall try to bring together a few physical effects in the literature, point out their relevance to the present problem and try to give a physically consistent microscopic picture of what is taking place.

The physical picture that we envision consists of the following. We assume that there are both d and f states at the Fermi surface. Because of the Coulomb attractive force between the d electron and the f hole in these compounds they can form an exciton and thus the system may actually be an excitonic insolator. However, if the attractive force is of too short a range, a bound electron-hole state may not form (according to Mott). We found here that for a contact non-spin-flip potential there is indeed no excitonic phase transition at any temperature $T \neq 0$. However, such excitonic effects can still show up in the resistivity. Because of the attractive Coulomb force the electron-hole pair stays together a long time in between hoppings from site to site. This enhances the probability amplitude of a d electron being scattered into an f state by an impurity and hence enhances the resistivity. The time that the d-f electron-hole pair stays together as one goes to lower and lower temperature towards excitonic instability (which occurs at $T = 0$) diverges in a power-law manner. Thus the resistivity increases as T is lowered. The large linear specific heat is probably owing just to the presence of the heavy f electrons at the Fermi surface and will not be very much discussed in the present paper.

This paper is organized as follows: In Sec. II the model Hamiltonian will be set up. The d-f density autocorrelation function is then calculated using the first-order renormalization-group technique. In Sec. III we discuss the effect of electron-electron interaction on the resistivity data and show how one can understand the apparently resistive behavior of the electrical conductivity. Comparison with experiment is made and the agreement is good.

II. PROBLEM

These rare-earth compounds normally are metallic (as is indicated by their large conductivity and metallic luster) with both f and d electrons near the Fermi surface, normally the f electrons are much heavier (see Sec. IV) than the d electrons. The f and the d electrons interact

with each other by both non-spin-flip (V_0) and spin-flip V_s Coulomb forces. We can write the Hamiltonian as

$$H = H_0 + H_1, \tag{1}$$

$$H_0 = \sum k d^\dagger_{k\sigma} d_{k\sigma}, \tag{2}$$

$$H_1 = \frac{g_1}{L}\sum f^\dagger_{K_4\sigma_1} d^\dagger_{k_3\sigma_2} f_{k_2\sigma_2} d_{k_1\sigma_1} - \frac{g_2}{L}\sum f^\dagger_{k_1\sigma_2} d^\dagger_{k_3\sigma_1} f_{k_2\sigma_2} d_{k_1\sigma_1}, \tag{3}$$

where we have assumed that both the d and the f electrons have a twofold spin degeneracy. This is certainly the case in SmB_6 and is an approximation in SmS. This is not essential and will not affect our final conclusions. Note that we have used an exchange interaction g_1 in H_1 rather than a $V_s \vec{\sigma}\cdot\vec{s}$ term. Kasuya[5] has shown that

$$V_s = -2g_1, \tag{4}$$

$$V_0 = -\tfrac{1}{2} g_1 + g_2. \tag{5}$$

We have not explicitly included a term $V_{df}(d^\dagger_k f_k + f^\dagger_k d_k)$ in our Hamiltonian. It turned out that V_{df} is very small. This point will be discussed further in Sec. IV. Lastly, we have not included any phonon effects in Eqs. (1)–(3). They are important in certain aspects of the problem but are not relevant here. This point will also be taken up in Sec. IV.

One of the important features of the problem is that the f holes are extremely heavy, so that they have a very large probability amplitude of exciting a lot of low lying d-electron-hole pairs. This is the result of a finite scattering matrix element and an extremely small energy denominator and has come to be known under the name of infrared catastrophe.[6,7] Infrared divergence also exists in other problems. For example, the renormalization-group method has been applied to the Kondo problem by Abrikosov and Migdal,[8]

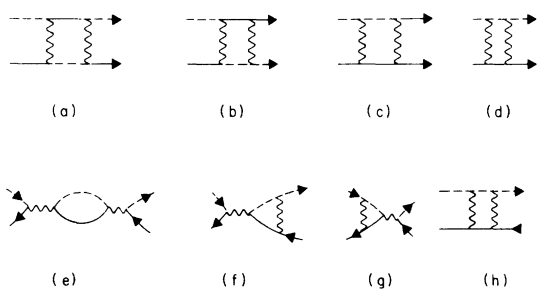

FIG. 1. All the second-order diagrams that contribute to the density autocorrelation function at momentum transfer $q = 2k_F$ in the 1-D Menyhard-Solyom model.

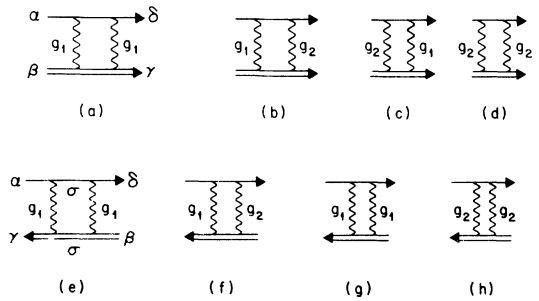

FIG. 2. All the second-order diagrams that contribute to the d-f density response function at zero momentum transfer, showing the equivalence to the 1-D Menyhard-Solyom model.

Fowler and Zawadowski,[9] and more recently by Solyom and Zawadowski.[10] This method has also been applied by Menyhard and Solyom[11] and Solyom[12] to the one-dimensional (1-D) interacting electron-gas problem. By writing H_1 in terms of g_1 and g_2 rather than V_s and V_0 the equivalence between the 1-D problem and our present one is apparent. (In the 1-D case, g_1 and g_2 correspond to electron-electron interaction with momentum transfer 0 and $2k_F$, respectively.) The lowest-order diagrams for the d-f T matrix are illustrated in Fig. 1. There is a one-to-one correspondence between these diagrams and their counterparts in the 1-D problem as is illustrated in Fig. 2.[13] For example, the contribution from Fig. 2(e) is

$$(1/2\pi v)[\ln(\omega/\omega_D) - \tfrac{1}{2} i\pi] 2g_1^2 \delta_{\alpha\gamma}\delta_{\beta\delta}.$$

The factor of 2 multiplying g_1^2 is due to the spin degeneracy of the bubble. Similarly, the diagram from Fig. 1(e) is

$$(1/\pi v)[\ln(\omega/\omega_D) - \tfrac{1}{2} i\pi] 2g_1^2 \delta_{\alpha\gamma}\delta_{\delta\beta}.$$

The exchange interaction only requires the spins of the incoming (outgoing) d and the outgoing (incoming) f electrons to be the same, leaving a spin degeneracy in the particle-hole intermediate state in Fig. 1(e), thus giving again an extra factor of 2. The factor of $1/\pi v$ instead of $1/2\pi v$ in front comes from the difference in the energy denominator in the two problems. One ends up with expressions like

$$\frac{1}{\pi}\int \frac{dq}{\omega - 2v_F q} \quad \text{and} \quad \frac{1}{\pi}\int \frac{dq}{\omega - v_F q}$$

in the 1-D and the present problem, respectively. Since only these first-order diagrams come into the first-order renormalization calculation, thus up to first-order renormalization, the T matrices Γ in the two problems are the same.

The equivalence of the two problems, as far as the "parquet" method is concerned, is also

obvious if one realizes that the corresponding diagrams in Figs. 1 and 2 are topologically the same. This can be seen by contracting all interaction lines into points and realizing that the corresponding vertices represent equivalent matrix elements. Writing the T matrix as

$$\Gamma_{\alpha\beta,\gamma\delta} = g_1\delta_{\gamma}\delta_{\beta\delta} - g_2\delta_{\alpha\delta}\delta_{\beta\gamma}, \tag{6}$$

we have, according to Refs. 11 and 12,

$$g_1(x) = \frac{g_1}{1-(2g_1/\pi v)\ln x}, \tag{7}$$

$$g_2(x) = +g_2 - \frac{g_1}{2} + \frac{1}{2}\left(\frac{g_1}{1-(2g_1/\pi v)\ln x}\right), \tag{8}$$

$$x = \ln(T/E_F), \tag{9}$$

and

$$\frac{\pi v}{2}\frac{\partial N_{df}}{\partial \ln\omega} = \left(1-\frac{2g_1}{\pi v}\ln x\right)^{-3/2} x^{\alpha}, \tag{10}$$

$$\alpha = (g_1 - 2g_2)/\pi v = -2V_0N(0). \tag{11}$$

Equations (7) and (8) are the same as that derived by Fowler and Zawadowski.[9] By using the equivalance to the 1-D problem, we have been able to obtain the d-f density autocorrelation function. The latter has not been derived by the authors of Ref. 9. Physically the present problem is different from the Kondo problem in the sense that we have both f electrons and holes. However, it only shows up in the fluctuation corrections and in higher-order renormalization calculations. From Eqs. (4), (5), (10), and (11) we conclude that (a) any kind of power-law dependence in the density autocorrelation function is produced by V_0, the spin-independent electron-electron interaction, alone. (b) Only V_s can cause a divergence in N at finite temperature; furthermore, this temperature is unaffected by V_0 at all.

The divergence of this correlation function indicates a possible phase transition. However, since V_s is much smaller than V_0, its effect will be overwhelmed by that of V_0 in the temperature range of interest. We shall therefore ignore it in what follows.

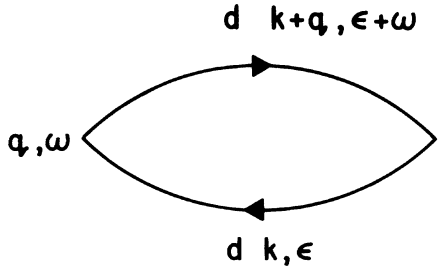

FIG. 3. Schematic d-d current autocorrelation function.

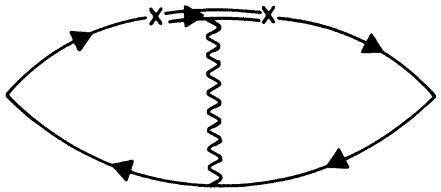

FIG. 4. Coulomb correction to the d-f impurity vertex in the d-d current autocorrelation function. It is diagrams of this type that contribute to the peculiar resistivity behavior observed in the rare-earth chalcogenides.

III. RESISTIVITY

In this section, we shall try to calculate the resistivity in the model that has been expounded in Sec. II. First of all, the conductivity is given by

$$\sigma = (Ne^2/m)\tau_{1t}. \tag{12}$$

The subscript t indicates a transport relaxation time. Because the current is carried mainly in the d electrons, one is mainly interested in the d electron current autocorrelation function as is illustrated in Fig. 3. The lifetime is dominated by the Coulomb-enhanced d-f impurity scattering as is illustrated in Fig. 4.

In order to evaluate the vertex corrections as in Fig. 4, we shall use a memory function technique developed by Götze and Wolfle.[14] Assuming a frequency dependence of the form $\alpha/(\omega+\tau^{-1})$ for the conductivity, they were able to obtain an approximate expression (to first order in the impurity concentration C) for the relaxation time:

$$\tau^{-1} = \gamma|V_i|^2\sum(v_k - v_{k'})^2\frac{\partial}{\partial\omega}\mathrm{Im}N_{kk'}, \tag{13}$$

where γ is a constant, V_i is the electron impurity potential, and N is the density autocorrelation function. Generalizing their formula to the present case, we obtain

$$\tau_{1\tau}^{-1} = \gamma'(\tau_{df}^0)^{-1}\left(\frac{1}{1-g_1\ln[(T+\beta\tau^{-1})/E_F]}\right)^{3/2} \times[(T+\beta\tau^{-1})/E_F]^{-\alpha}. \tag{14}$$

γ' and β are constants. Note that we have $(T+\beta\tau^{-1})/E_F$ rather that T/E_F, as one expects from the above consideration. The introduction of the additional term $\beta\tau^{-1}$ with a numerical coefficient β should be regarded as phenomenological and is based on the following physical consideration. The quantity $x = T/E_F$ is a measure of the sharpness of the Fermi surface. Obviously, impurity also smears the Fermi surface and one should

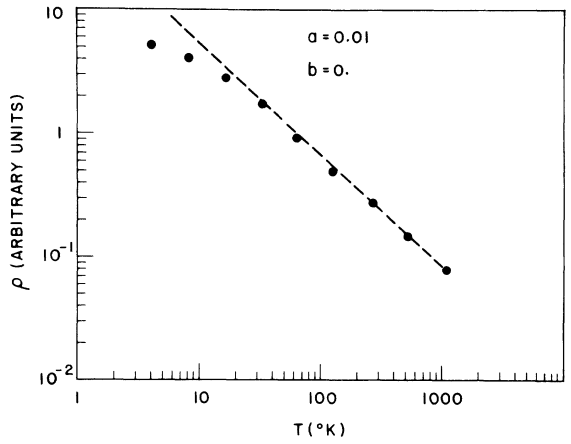

FIG. 5. Model calculation of the resistivity. y axis is essentially τ^{-1} which is obtained by solving the simplified equation $\tau^{-1}=\tau_0^{-1}[T+\tau^{-1}/E_F]^{\alpha}$, $\tau_0=a+bT$, E_F = 1000 °K. Here b is set equal to zero but a remains finite, $\alpha = 0.9$. Rounding off of the resistivity at low temperature is illustrated.

expect that τ^{-1} should come in as the lower limit cutoff when T is much less than it. A simpler version of this (with $g_1 = 0$ and without calculating τ self-consistently) has been given by the author.[15] When τ_0^{-1} is large enough, σ does not follow a simple power law. We have performed model calculations of τ^{-1} assuming that τ_0^{-1} is of the form $a+bT$, the temperature-dependent term being due to phonons. The results are plotted in Figs. 5–7 for different values of a and b. The general conclusion is that σ becomes less and less power-law-like for small T as a gets larger and larger. Similarly, the slope bends over for large T as b becomes bigger and bigger. This seems to be also the case experimentally. In Figs. 8–11 we have plotted the resistivity of SmB_6,[1] and "metallic"

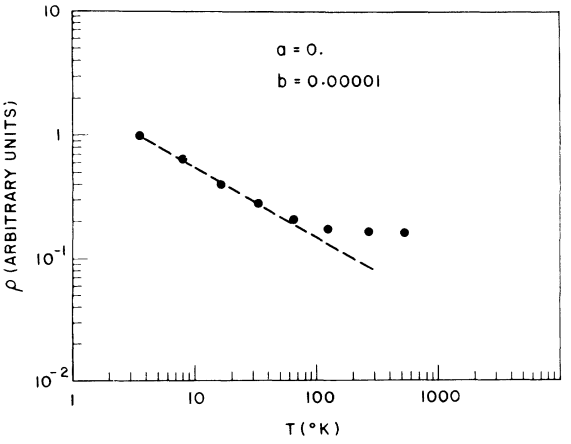

FIG. 6. Model calculation of the resistivity with a = 0 but b finite. Showing the upward slope of the resistivity at higher temperatures.

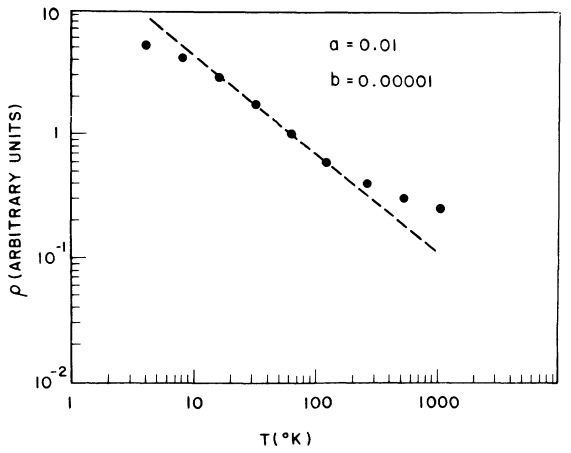

FIG. 7. Model calculation of the resistivity with both a and b finite.

SmS,[4] TmS, and TmSe,[16] on a logarithmic scale. They all fall on a straight line at intermediate values of T. As can be noted, metallic SmS and TmSe has a smaller resistivity and is much more "power-law-like," whereas SmB_6 and TmS has a larger resistivity and hence is much less "power-law-like," looking very much like the curves in Fig. 7.[17] The exponents α that we deduce from these curves are 0.98, 0.58, 0.33, and 0.45, for SmB_6, metallic SmS, TmSe, and TmS, respectively. Note that α is *not* an integer. It is difficult to imagine that any other kind of ordinary theory will be able to explain this.

IV. CONCLUSION

A summary of what we have reported in this paper is already given in the abstract. More points should be noted. First of all, the discussion of the impurity effect here should be also applicable to the one-dimensional problem. The second point is about phonons. In a previous publication, Anderson and Chiu[18] have argued about the im-

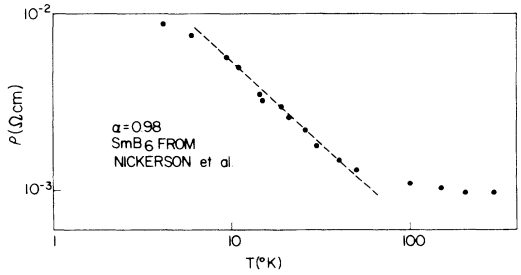

FIG. 8. Experimental data of the resistivity of Nickerson *et al.* on SmB_6 on a logarithmic scale. Note the three portions of the curve corresponding to high, low, and intermediate temperatures and compare this to Fig. 7.

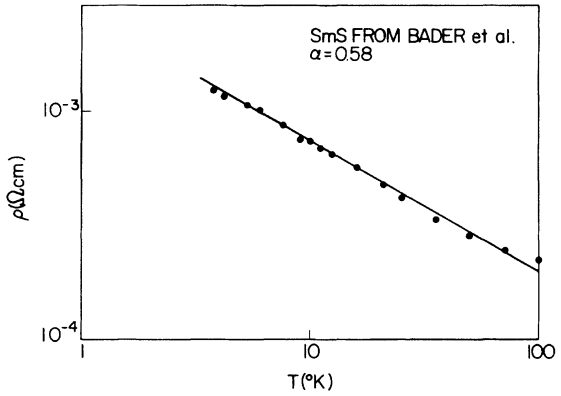

FIG. 9. Log-log plot of the resistivity data of Bader *et al*. for SmS at 10 kbar.

portance of anharmonic phonons in stabilizing a mixed valence state. Sherrington and von Molner[19] have also pointed out that, in trying to relate the Kondo-Ruderman-Kittel-Yosida exchange term J to the Anderson-Friedel hybridization energies, phonon overlap greatly reduced J relative to V. We have examined what further effects these will have and find that once we fix J (or g_1, g_2), phonons affect σ only in that they affect τ_0^{-1} and m^*. (V_{df} is reduced.)

Thirdly, our model Hamiltonian should contain a term $V_{df}(d_k^\dagger f + f^\dagger d_k)$. In a sense, our calculating τ^{-1} self-consistently is a phenomenological treatment of this effect. The V_{df} term also contributes to τ.

This will be adequate so long as V_{df} is not very large. The effect of V_{df} can be estimated as follows. Because of V_{df} the f band now has a finite mass as is illustrated in the self-energy correction in Fig. 12. Note that this self-energy correction is *not* modified by the Coulomb interactions; owing to the instantaneous nature of the Coulomb force, such diagrams as in Fig. 13 are not possible.

This finite f mass is manifested in a large γ for the specific heat. In SmS, this is about 100

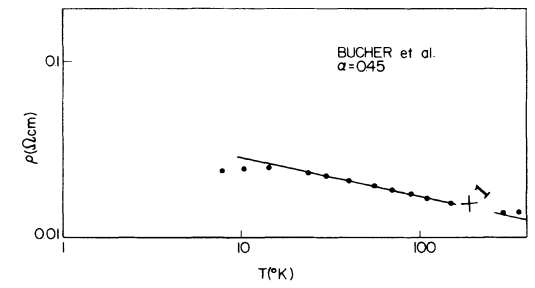

FIG. 10. Log-log plot of the resistivity data of Bucher *et al*. for TmS.

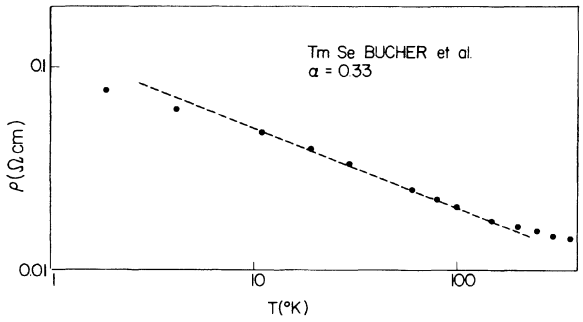

FIG. 11. Log-log plot of the resistivity data of Bucher *et al*. for TmSe.

times that of copper. Taking a d bandwidth of the order of 1 eV, we have

$$\frac{N}{N_0}\ \frac{1}{T_F(f)} = 100\,\frac{1}{T_F(d)}\,,$$

where N/N_0 is the number of electrons per atom. This is about 0.17 for "metallic" SmS. Here $T_F(f)$ and $T_F(d)$ stand for the Fermi temperature of the d and the f electrons, respectively. We thus have

$$T_F(f) \simeq 17\,^\circ\mathrm{K},$$

a very small number indeed. [Compare this with the Fermi temperature of the d electrons— it is $(T+\tau^{-1})/E_F$ that appears in our formulas.]

Mott[20] has recently proposed that perhaps a gap may exist in "metallic" SmS and SmB_6. We find it difficult to reconcile his idea with the low-temperature specific-heat[1,4] data which show a linear temperature-dependent part. Furthermore, we have plotted the $\ln\rho$-vs-$1/T$ curve for the data of both Refs. 1 and 4. We find that they do not lie on a straight line. In any case, if we blindly calculate the slope of the lowest T portion of these curves, we find a gap of the value 1.6 °K and 1.34 °K for SmB_6 and SmS at 10 kbar, respectively. For a small value of the gap, the d-f scattering effect that we discussed in this paper will still come in. In that case, the relevant parameter will not be $(T+\beta\tau^{-1})/E_F$ but $(T+\beta\tau^{-1}+b\Delta)/E_F$, where b is a coefficient on the order of unity.

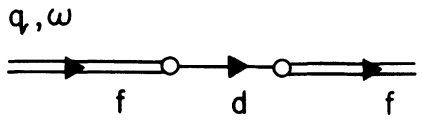

FIG. 12. First-order diagram showing the self-energy correction to the f electrons owing to a d-f mixing term V_{df}.

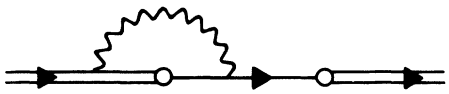

FIG. 13. Diagram illustrating that it is not possible to have Coulomb vertex corrections to Fig. 12 because of its instantaneous nature.

As we see, this effect has rather serious consequences and has been totally neglected in Mott's discussion.

ACKNOWLEDGMENTS

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*Present address.

[1]There have been many experiments done on this material and it is not possible to give proper credit and list all the references. See, e.g., the article by J. C. Nickerson, R. M. White, K. N. Lee, R. Bachman, T. H. Geballe, and G. W. Hull, Jr., Phys. Rev. B 3, 2030 (1971), and references therein.

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