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ANTIFERROMAGNETIC ENERGY GAP IN CHROMIUM

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A temperature-dependent dip has been observed in the infrared reflectivity of chromium, which is attributed to excitation of an electron across the antiferromagnetic energy gap. At 80°K, the absorption maximum occurs at photon energy $5.1kT_N$, which is larger than the value predicted by the simplest BCS-type model, $3.5kT_N$. Both the position and shape of the absorption can be explained if the effects of electron-phonon scattering are incorporated in the model.

This Letter reports the first observation of the optical energy gap in an itinerant-electron antiferromagnet. The shape and position of the absorption curve are found to be in good agreement with a simple model which includes electron-phonon scattering as well as the usual electron-electron interaction.

The itinerant electron theory of antiferromagnetism, first applied to chromium by Lomer[1] and Overhauser,[2] predicts a temperature-dependent gap in the electron-energy spectrum below the Néel temperature ($T_N = 312$°K), which removes a portion of the Fermi surface[3] and should lead to an absorption threshold in the infrared. The photon energy at this threshold, according to the simplest BCS-like model, would be $3.5kT_N$.[2] Previous optical measurements by other workers, on bulk polycrystalline samples and on films, showed no temperature-dependent structure.[4]

In the present experiments, single-crystal chromium samples (resistance ratio 200) were spark cut to expose a flat face, and then were mechanically polished. After a polishing etch in perchloric acid, the samples were arranged as shown in Fig. 1 to allow three reflections of the infrared beam. Measurements were made relative to one reflection from aluminum and were then corrected for the known reflection of aluminum. Figure 1 shows the R^3 spectrum of chromium. The major temperature-dependent feature is a broad dip near 1000 cm^{-1}. This dip shifts to lower energy and weakens as the temperature is increased. The dip has disappeared at 300°K. A measurement above T_N shows only very small changes from the 300°K data. The reflectivity minimum near 5000 cm^{-1} is thought to be a regular band-structure feature and is unaffected by the antiferromagnetic transition. A small dip in the reflectivity near 600 cm^{-1} is also present at all temperatures and is currently unexplained.

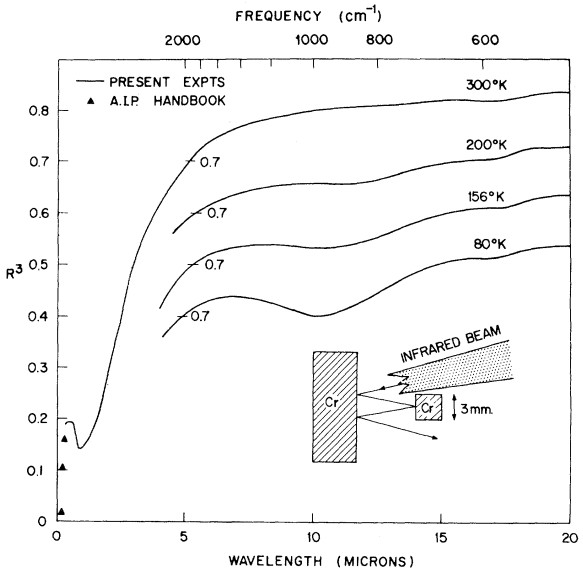

FIG. 1. Cube of the reflectivity of chromium. The three lower curves are vertically displaced as indicated. The insert shows sample arrangement.

We have assumed that the electromagnetic response of the chromium is given by a local frequency-dependent conductivity $\sigma(\omega)$, characteristic of the bulk metal (i.e., normal skin effect). The data shown in Fig. 1 can then be analyzed, using the Kramers-Kronig relations, to obtain $\sigma(\omega)$, the real part of which, σ', is plotted in Fig. 2 for three different temperatures. In order to study the antiferromagnetic absorption peak, near 1000 cm^{-1}, it is necessary to

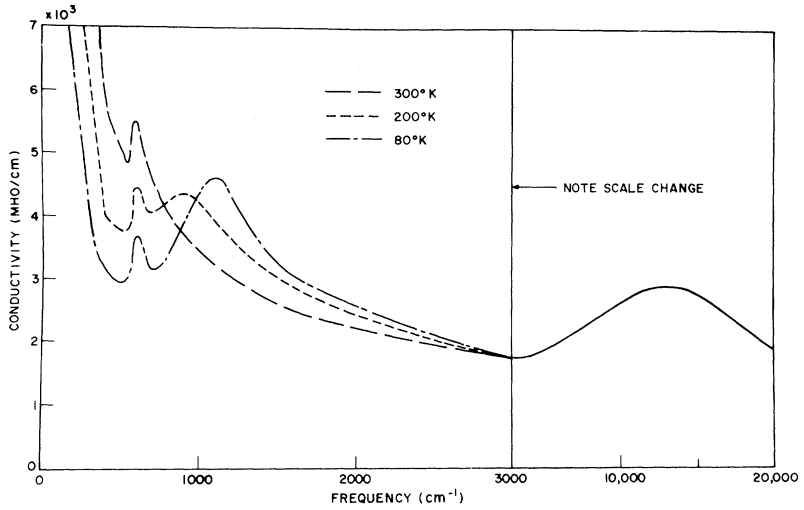

FIG. 2. Conductivity function for chromium. Curves show the real part of the conductivity obtained by Kramers-Kronig analysis of the reflectivity at three different temperatures.

subtract from the total conductivity the "background" conductivity due to free-carrier absorption. The problem here is similar to that in nickel discussed by Ehrenreich, Philipp, and Olechna.[5] The known dc conductivity is much larger than σ' observed in the infrared, and the falloff of σ' is not of Drude form. Thus it is difficult to separate out theoretically the free-carrier part of σ'.

In order to proceed we must make some simplifying assumptions. We have assumed that at 300°K, all absorption below 2000 cm^{-1} is due to free carriers. At 80°K, we assume that $\sigma'(\omega)$ is the sum of an antiferromagnetic part and a free carrier part. The free carrier part we assume to be proportional to $\sigma_{300°K}'$, but reduced in over-all magnitude because of the antiferromagnetic energy gap which causes carriers to freeze out over part of the Fermi surface. We calculate the antiferromagnetic part of $\sigma_{80°K}'$ by

$$\Delta\sigma_{exp}' = \sigma_{80°K}' - c\sigma_{300°K}',$$

where we have $c = 0.53 \pm 0.10$, if we wish to make $\Delta\sigma_{exp}'$ go to zero at some frequency in the range 300 to 600 cm^{-1}. The curve for $\Delta\sigma_{exp}'$ is plotted in Fig. 3. It is an asymmetric curve, with a maximum at 1100 cm^{-1} ($\hbar\omega = 5.1kT_N$). The position of the maximum is not sensitive to the details of the subtraction process. Typical uncertainties in $\Delta\sigma_{exp}'$ which result from the arbitrariness in choosing c are indicated in Fig. 3 by error bars. At frequencies between 3000 and 14 000 cm^{-1} we find that $\sigma'(\omega)$ increases with increasing frequency, an effect which may be attributed to interband absorption. (Nonrelativistic calculations of the band structure[1,6] predict a band degeneracy along the [100] direction, leading to nonvanishing interband transitions at arbitrarily low frequencies.) The temperature-independent contribution of interband transitions probably invalidates our subtraction procedure above 2000 cm^{-1}, leading to calculated values of $\Delta\sigma_{exp}'$ which are larger than the true antiferromagnetic part in this

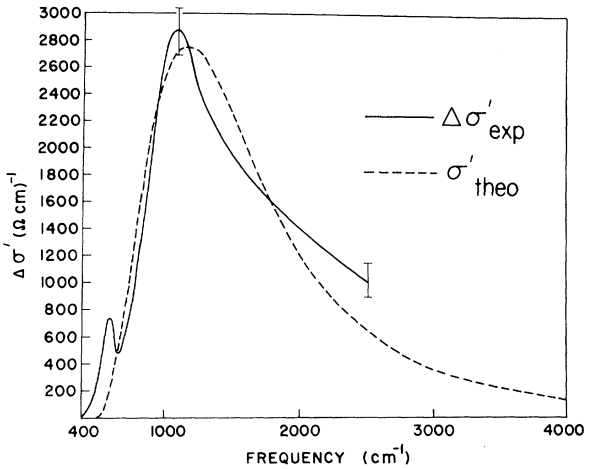

FIG. 3. "Antiferromagnetic" part of σ'. The solid curve shows $\Delta\sigma_{exp}' = \sigma_{80°K}' - 0.53\sigma_{300°K}'$. The subtraction procedure leaves a small part of the temperature-independent peak at 600 cm^{-1}. Error bars indicate estimated uncertainties due to the choice of constant in the subtraction procedure. The dashed curve shows the theoretical antiferromagnetic absorption σ_{theor}' described in the text.

region. The area under the curve $\Delta\sigma_{exp}'$ above 400 cm^{-1} is found to be approximately $\frac{1}{3}$ the area under $\sigma_{300°K}'$ between 0 and 2000 cm^{-1}. If we assume that the Fermi velocity is constant over the Fermi surface, this indicates that $\frac{1}{3}$ of the Fermi-surface area is involved in the antiferromagnetic transition. This fraction is consistent with previous estimates of $\frac{3}{10}$ and $\frac{1}{2}$ based on dc conductivities[7] and on low-temperature specific heat measurements,[8] respectively.

A simplified model for the itinerant antiferromagnetism in chromium has been studied by Fedders and Martin.[9] The magnetic portions of the Fermi surface are represented by a spherical electron surface and a spherical hole surface, having the same radii k_F, but centered at different points of the Brillouin zone. Because the electron and hole surfaces are identical in shape, one finds at 0°K that the Fermi surface would be unstable to the formation of bound electron-hole pairs, for arbitrarily weak attractive interaction between electrons and holes. It is the condensation of triplet electron-hole pairs which is responsible for the antiferromagnetism.

We shall assume that the effective masses of the electrons and holes have the same value m, and that the electron-hole attraction is small compared with the Fermi energy and is independent of wave vector, for momentum transfers less than $2k_F$. When this model is treated in the Hartree-Fock approximation, it is mathematically identical to the BCS model of superconductivity. Below T_N there is a gap 2Δ in the quasiparticle spectrum, where $\Delta(T)$ is given by the BCS gap function, and $2\Delta(0) = 3.5kT_N$. The value of $\Delta(0)$ is only weakly dependent on details of the model, such as the assumption of equal masses for the electrons and holes.

The absorptive part of the conductivity has the form[9]

$$\sigma'(\omega) = \frac{4e^2k_F^3}{3\pi m\hbar}\,\frac{\Delta^2}{\omega^2}\,\frac{\tanh(\hbar\omega/4kT)}{[(\hbar\omega)^2-(2\Delta)^2]^{1/2}} \qquad (1)$$

for $|\hbar\omega| > (2\Delta)$. In addition there is a δ-function "free carrier" contribution at $\omega = 0$, whose magnitude is determined by the f sum rule condition on the integral of $\sigma'(\omega)$. The free-carrier contribution from the magnetic part of the Fermi surface vanishes at 0°K.

When scattering of electrons by phonons is taken into account, the δ function at the origin will be broadened into a Drude-type peak. The antiferromagnetic absorption will also be broadened, and the infinity in σ' at $\hbar\omega = 2\Delta$ will be removed. (In real chromium, the antiferromagnetic absorption will also be broadened because the effective interaction will be wave vector dependent, and the energy gap will not be constant over the magnetic part of the Fermi surface.) The peak position will also be affected by the phonons and will no longer occur at the energy gap.

The strength of the electron-phonon interaction can be obtained from the mass renormalization factor due to electron-phonon interactions, which has been calculated by McMillan for various superconducting transition-metal alloys, and has been extrapolated to give $m^*/m = 1.25$ for the hypothetical paramagnetic ground state of pure Cr.[10] This determines the electron-phonon scattering lifetime at high temperatures to be[11]

$$\hbar/\tau = 1.57kT. \qquad (2)$$

At 0°K the scattering lifetime is energy dependent, but for electron energies greater than the Debye energy, we have (in the paramagnetic state)

$$\hbar/\tau = 1.57\hbar\omega_0/2, \qquad (3)$$

where ω_0 is a typical phonon energy which we take to be 35 meV.[12] We shall replace the energy-dependent lifetimes by an energy-independent lifetime whose value is given by Eq. (2) at $T = T_N$ and by Eq. (3) at $T = 0$, i.e., $\hbar/\tau k = 490$ and 320°K, respectively. We may obtain an upper bound (and probably a reasonable approximation) to the effects of the phonons by assuming that there is no scattering between the electron portion of the Fermi surface and the hole portion, that the scattering is isotropic within each portion, and that the electron-phonon coupling constants have the same values in both regions of the Fermi surface. The phonons are now mathematically equivalent to random impurity potentials which have opposite signs for electrons and holes, and they have a depairing effect similar to that of magnetic impurities in superconductors. Using Green's function methods, Zittartz[13,14] has calculated effects of impurities on the Fedders-Martin model. The depairing leads to a renormalization of T_N and of the function $\Delta(T)$. From Eq. (56) of Ref. 13, we calculate the "unrenormalized" Néel temperature, $T_N^0 = 750°K$,

for a model without phonon scattering, which will just give the observed $T_N = 312°K$ when scattering is added with $\hbar/\tau k = 490°K$. Using this T_N^0 and the zero-temperature scattering $\hbar/\tau k = 320°K$, we may calculate $\Delta(0)$ and the conductivity $\sigma_{theor}'(\omega)$ at 0°K. (The calculation procedure for σ' is very similar to the procedure used by Zittartz for the dc conductivity.[14]) The maximum in σ_{theor}' is found to occur at 1200 cm^{-1}.

The curve σ_{theor}' is compared with $\Delta\sigma_{exp}'$ in Fig. 3. (We do not expect much difference between 0 and 80°K.) The normalization of the curve σ_{theor}' depends on the unknown parameter k_F^3/m, and we have chosen the normalization to give approximately the same area as that found for $\Delta\sigma_{exp}'$. The normalization is the only adjustable parameter in σ_{theor}', however, and the agreement between σ_{theor}' and $\Delta\sigma_{exp}'$, with respect to shape and peak position, is remarkably good, in view of the many simplifying approximations we have made.

We have measured σ' experimentally at 156 and 200°K as well as at 80°K. Although we have not calculated σ' at these higher temperatures, the experimentally observed decrease in magnitude of the antiferromagnetic absorption mode and shift of peak position towards lower energy are in at least qualitative agreement with the theory.

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SUPERCONDUCTIVITY IN MULTIPLE PAIR-BREAKING REGIMES*

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It is found experimentally that the thermodynamic behavior of superconductors in multiple pair-breaking regimes can be described by a particularly simple formalism due to Abrikosov and Gor'kov, and Fulde and Maki.

The major theoretical breakthrough in the problem of superconductivity in the presence of pair-breaking perturbations was made by Abrikosov and Gor'kov (AG).[1] Their theory explained the results of the experiments of Matthias, Suhl, and Corenzwit[2] on the lowering of T_c of superconductors with magnetic impurities. It has since been realized that the AG theory can be extended to treat other pair-breaking situations which lead to second-order superconducting-normal phase transitions.[3] Examples of these are the vortex state, the surface sheath state, the proximity effect (thin superconductors in contact with magnetic or nonmagnetic normal metals), small superconductors in magnetic fields, and superconductivity in the presence of strong Pauli paramagnetism.

The well-known equation from the AG theory which describes the (second-order) superconducting-normal (s-n) phase boundary of a superconductor with magnetic impurities may be written in the form

$$\ln\frac{T}{T_{c0}} + \psi\left(\tfrac{1}{2} + 0.14\frac{T_{c0}}{T}\frac{\alpha}{\alpha_{cr}}\right) - \psi(\tfrac{1}{2}) = 0, \qquad (1)$$