# PRESSURE DEPENDENCE OF ITINERANT ANTIFERROMAGNETISM IN CHROMIUM

D. B. McWhan and T. M. Rice
Bell Telephone Laboratories, Murray Hill, New Jersey
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The Néel temperature of Cr is found to vary exponentially with volume, which is in support of a two-band model of itinerant antiferromagnetism. The temperature dependence of the magnetic contribution to the electrical resistivity can be explained by taking into account only the variation in the number of effective carriers from the introduction of a band gap ($2\Delta$) due to the magnetic ordering. The ratio $\Delta_0/kT_N$ is estimated at 2.3 at $P = 26$ kbar.

The electrical resistance of chromium has been measured from 4.2 or 77 to 298°K at different pressures up to 82 kbar. The volume dependence of the Néel temperature (Fig. 1) shows strong curvature in marked contrast to the magnetic ordering temperatures of Ni,[1] Fe,[2] Invar,[2] and the rare-earth metals[3] which are linear over the same volume change. These results and the magnetic contribution to the resistivity are interpreted using the itinerant two-band model of antiferromagnetism due to Lomer[4] and Overhauser.[5] This model has had considerable success in interpreting many properties of Cr.[6,7]

Three samples of single-crystal chromium (Battelle Iochrome) were used with samples 2 and 3 being from the same ingot. The high-pressure measurements were made in a girdle die using AgCl as the pressure-transmitting medium; the apparatus has been described elsewhere.[3,8] The pressure calibration is relative to the transitions in a bismuth wire mounted in the cell and assumes a linear relation between applied load and pressure with fixed points at the origin, 25.4 kbar (Bi I-II), and 80 kbar (Bi III-V). The error in $P$ is $\approx 3\%$. The temperature was measured with a thermocouple mounted on the girdle, and in addition for sample 3 a thermocouple was put in the cell. The temperature of the girdle lags behind the sample, and a 2°K correction was applied to the data for samples 1 and 2. With sample 1 there were large temperature gradients in the apparatus and the uncertainty in $T_N$ is shown in Fig. 1. A series of isobars of the resistance, measured by a four-lead method, were made. The pressure was increased near room temperature where AgCl has a low yield strength.

There was a negligible change in $T_N$ and the resistance anomaly observed at 1 atm before and after the pressure experiment, and this suggests that the lack of true hydrostatic conditions does not affect the validity of the experiments. The resistivity ratios before and after were the following: $R_{298}/R_{4.2} = 535$ (1) and 275 (3) (before) and 180 (1), 140 (2), and 165 (3) (after). The pressure cycle produced a 3-7% permanent elongation of the samples. Figure 2 shows the curves of $R/R(1\text{ atm}, 298)$ vs $T$ for samples 2 and 3 and demonstrates the reproducibility of the experiments. In Fig. 1 the volume change was calculated using the one-parameter Birch equation[9] with a bulk modulus ($B_0$) of 1620 kbar.[10]

The data of Fig. 1 are fitted empirically by the equation

$$\ln\left(\frac{T_N(V)}{T_N(V_0)}\right) = \frac{B_0}{T_{N_0}}\left(\frac{dT_N}{dP}\right)_{P\to 0}\left(\frac{V_0 - V}{V_0}\right) = -26.5\left(\frac{V_0 - V}{V_0}\right), \quad (1)$$

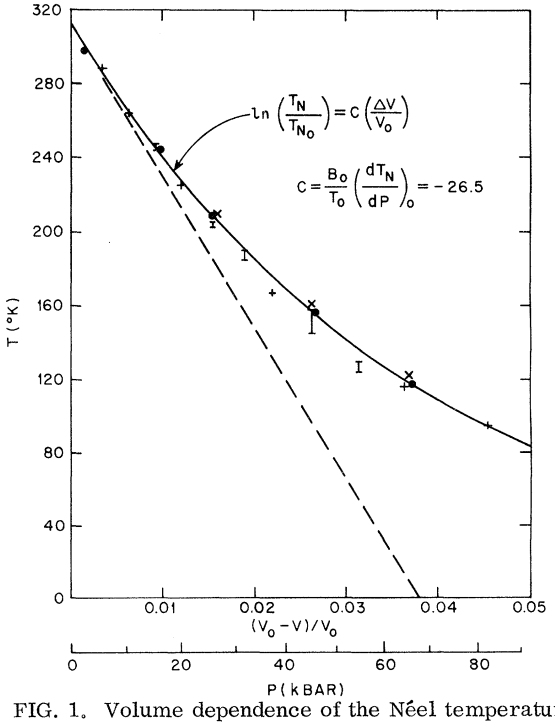


FIG. 1. Volume dependence of the Néel temperature of chromium. Vertical bars, sample 1; crosses, sample 2; and solid circles, sample 3.

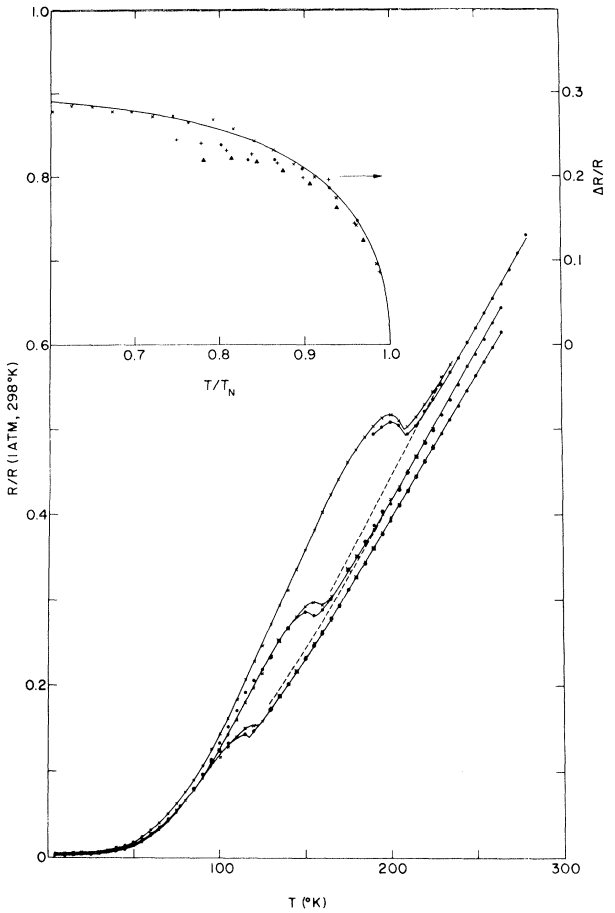


FIG. 2. Resistance versus temperature for sample 2 (crosses) and sample 3 (solid circles). From the top, the pressures are 26.5, 45.7, and 64.9 kbar for sample 2 and 26.3, 45.9, and 65.9 for sample 3. The dashed curve is the extrapolated paramagnetic resistance ($R_p$). The inset gives $\Delta R/R = (R_a - R_p)/R_a$ vs $T$. The solid curve is calculated using Eqs. (5) and (6) with $(\sigma_{2p}/\sigma_p)_{T=0} = 0.3$ and $\Delta_0/kT_N = 2.3$. Crosses and solid triangles: sample 2 at 26.5 and 45.7 kbar, respectively; solid circles: sample 3 at 45.9 kbar; plus signs: sample 1 at 45.7 kbar.

and $T_{N_0} = 312°K$ and $(dT_N/dP)_{P\to 0} = -5.1°K/kbar$.[11] This exponential dependence seems to differ from that found in the one-band model,[12] but it is compatible with the two-band itinerant model of antiferromagnetism.[4-6] We assume that the electron Fermi surface and the hole Fermi surface displaced by the spin-density wave vector $\vec{Q}$ match well so that

$$|\xi_{\vec{k}}| = |\tfrac{1}{2}[\epsilon^e(\vec{k}) - \epsilon^h(\vec{k}+\vec{Q})]| < k_B T_N$$

for $\vec{k}$ on $A_M$. $A_M$ is some finite area of the Fermi surface which we shall refer to as the "magnetic" part. Under these circumstances the transition temperature will be determined by a Bardeen-Cooper-Schrieffer equation and the antiferromagnetic phase will have a temperature-dependent gap over the "magnetic" part of the Fermi surface. In this model $T_N$ is given by[13]

$$T_N = T_B \exp(-1/\lambda), \tag{2}$$

where $kT_B$ is of the order of the bandwidth and $\lambda = \gamma^2 V(0) A_M/8\pi^3 v$. In this equation $\gamma$ is an average matrix element, $V(0)$ the screened Coulomb interaction at $\vec{q}=0$, and $v$ is the average of the velocities in the electron and hole pockets. Equation (2) is compatible with Eq. (1) if $1/\lambda$ is expanded as a linear function of $(V_0 - V)/V_0$ and if $T_B$ does not vary rapidly with volume. It is difficult to make a meaningful estimate of the expected functional form of the volume dependence of the parameters that enter $\lambda$ and no attempt to define more than the leading term has been made.

We propose that the rapid change in $\lambda$ as a function of volume is due to a rapid shrinkage of $A_M$ as the volume decreases. This proposition can be tested by examining the electronic Grüneisen parameter[14] which gives the logarithmic volume derivative of the electronic specific heat at low temperatures, $\gamma_a$. In Cr this is anomalously large and negative. If $\gamma_a = \gamma_p - \gamma'$, where $\gamma_p$ is the density of states of paramagnetic Cr, then $\gamma'$, the density of states in the "magnetic" part, should scale approximately with $\lambda$ as a function of volume. Using $\gamma_a/\gamma_p = \frac{1}{2}$ at $P = 1$ atm,[15] one obtains

$$\frac{d\ln\gamma'}{d\ln V} = \frac{\gamma_p}{\gamma'}\frac{d\ln\gamma_p}{d\ln V} - \frac{\gamma_a}{\gamma'}\frac{d\ln\gamma_a}{d\ln V} = 10.5 \pm 2, \tag{3}$$

where $d\ln\gamma_p/d\ln V = 1 \pm 1$ was assumed, which is typical of Mo (1.6) and W (0.2).[14]

By Eqs. (1) and (2),

$$d\ln\lambda/d\ln V = 26.5\lambda = 9.3 \pm 1.5, \tag{4}$$

where we have taken $\lambda = 0.35 \pm 0.05$. It is very difficult to estimate $\lambda$ or $T_B$ accurately, and we have used $\lambda \approx \mu\gamma_a/\gamma_p$, where $\mu$ is the average of the Coulomb interaction times the density of states. $\mu$ has been estimated by Bucher and Andres[16] from studies of the Cr-Mo alloy system at $\mu = 0.7 \pm 0.1$. The good numerical agreement between Eqs. (3) and (4) is probably fortuitious but does seem to bear out our qualitative explanation. This value of $\lambda$ gives $k_B T_B = 0.5$ eV, which is smaller than the the-

oretical bandwidth. If we took $k_B T_B = 2$ eV,[17] then we would have $\lambda = 0.23$ and $d\ln\lambda/d\ln V = 6$.

The behavior of $T_N$ raises the interesting question as to whether Cr will be antiferromagnetic at zero temperature at all pressures. Equation (2) was derived assuming $|\xi_k| < k_B T_N$ over an appreciable fraction of the Fermi surface, and when this condition breaks down, then the transition temperature should drop rapidly to zero. It can be shown[18] that for a simple band-structure model, $dT_N/dV \to +\infty$ as $T_N \to 0$. However, for more irregular Fermi surfaces it is possible to have $dT_N/dV$ finite as $T_N \to 0$. To the highest pressures studied no departure from an exponential was found.

In Fig. 2 the resistance is plotted as a function of temperature at different pressures. If the lowest curve is scaled by multiplying it by a constant factor, then it lies quite well on the upper curves for $T \gg T_N$. The continuation for $T < T_N$, shown as the dashed curve in Fig. 2, gives an estimate of the paramagnetic contribution to the resistivity $R_p$. If one assumes that the Fermi surface is divided into two parts, then the conductivity can be written as $\sigma = \sigma_1 + \sigma_2$, where $\sigma_1$ is the contribution from the "nonmagnetic" part of the Fermi surface and $\sigma_2$ is the contribution from the "magnetic" part. The fraction of the resistance resulting from magnetic effects is then

$$\frac{\Delta R}{R_a} = \frac{R_a - R_p}{R_a} = \frac{\sigma_p - \sigma_a}{\sigma_p} = \frac{\sigma_{2p} - \sigma_{2a}}{\sigma_1 + \sigma_{2p}}. \tag{5}$$

It is assumed that the relaxation times are unaffected by the transition and that $\sigma_1$ is unchanged by the magnetic ordering. The ratio of $\sigma_2$ in the antiferromagnetic and paramagnetic phases is given by

$$\frac{\sigma_{2a}}{\sigma_{2p}} = \left( \sum_{\vec{k} \text{ on } A_i} \frac{\partial^2 E}{\partial k_i \partial k_i} \hat{n}_i^2 \frac{1}{e^{\beta E} + 1} \right) \Bigg/ \sum_{\vec{k} \text{ on } A_i} v_i^2 \hat{n}_i^2 \delta(\epsilon(\vec{k}) - \mu) = \int_{-\infty}^{+\infty} d\xi \frac{\Delta^2}{E^{\frac{3}{2}}} \frac{1}{e^{\beta E} + 1}, \tag{6}$$

where $\hat{n}$ is a unit vector, $\vec{v}$ is the velocity, and $E^2 = \xi^2 + \Delta^2$ with $2\Delta(T)$ the temperature-dependent gap introduced by the antiferromagnetic ordering.[19] The temperature dependence of $\Delta R/R$ is shown in the inset in Fig. 2 and the solid line is calculated using Eq. (6). Equation (6) has two adjustable parameters and a good fit was obtained for the data at $P = 26.6$ kbar and $T_N = 208°$K using $(\sigma_{2p}/\sigma_p)_{T=0} = 0.3$ and $\Delta(T=0)/kT_N = 2.3$. If a uniform relaxation time and density of states is assumed over the whole Fermi surface, then $\sigma_{2p}/\sigma_p = \gamma_a/\gamma_p$. The value of 0.3 is smaller than the value of 0.5 estimated by Heiniger, Bucher, and Müller.[15] The ratio $\sigma_{2p}/\sigma_p$ tends to decrease slightly as the pressure is increased, but our data are not accurate enough to derive any definite value for the rate of decrease.

It is difficult to estimate the accuracy of $\Delta_0/kT_N$ because the following implicit assumptions have been made: (1) The model for Cr assumes a multidomain structure and a second-order transition. It is known that Cr has a small first-order transition[20] which was not observed. (2) The resistance appears to have a precursor which extends to temperatures considerably above $T_N$[21] and this was ignored in computing $\Delta R/R$. This value is in agreement with $\Delta_0/kT_N = 2.2$ obtained by Trego and Mackintosh[22] from studies of the thermopower of Cr alloys.

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## POLARIZATION AND INTENSITY OF RAMAN SCATTERING FROM PLASMONS AND PHONONS IN GALLIUM ARSENIDE

A. Mooradian and A. L. McWhorter
Lincoln Laboratory,* Massachusetts Institute of Technology, Lexington, Massachusetts
(Received 7 July 1967)

Raman scattering from plasmons and phonons in GaAs has recently been reported[1] in which the coupling between the longitudinal optic phonon modes and the longitudinal plasma modes was demonstrated. We report here the investigation of the polarization properties and relative intensities of the Raman-scattered light from these mixed plasmon-phonon modes in oriented single crystals of $n$-type GaAs. The results are in good agreement with theoretical predictions[2] and yield values for the Raman tensor and electro-optic coefficient of GaAs.

A neodymium-doped yttrium aluminum garnet laser with a cw output of 3 W at 1.06 $\mu$ was used to excite the collective excitations. The experimental arrangement has been described previously.[1] The samples were rectangular parallelepipeds $3 \times 3 \times 7$ mm in size with {100} faces, and were mounted on a cold finger in contact with liquid helium. The laser beam, after passing through a polarizer, was incident along a ⟨100⟩ axis of the crystal while the scattered light was collected at 90° along another ⟨100⟩ axis. The solid angle of collection was about 0.08 sr. The system response was determined as a function of polarization and wavelength by using a calibrated quartz-iodine light source.

Figure 1 is a plot of the Raman frequency shifts as a function of the square root of the electron concentration and shows the mixing between the longitudinal optic phonon mode of frequency $\omega_l$ and the longitudinal plasma mode of frequency $\omega_p = (4\pi e^2/\epsilon_\infty m^*)^{1/2}$. Here $n$ is the electron concentration, $m^*$ the conduction-band effective mass, and $\epsilon_\infty$ the optical dielectric constant. The Raman line shapes and polarization properties for a sample with $n = 1.9 \times 10^{18}$ cm$^{-3}$ are shown in Fig. 2. The transverse optic (TO) mode at frequency $\omega_t$ is unaffected by the presence of the free car-

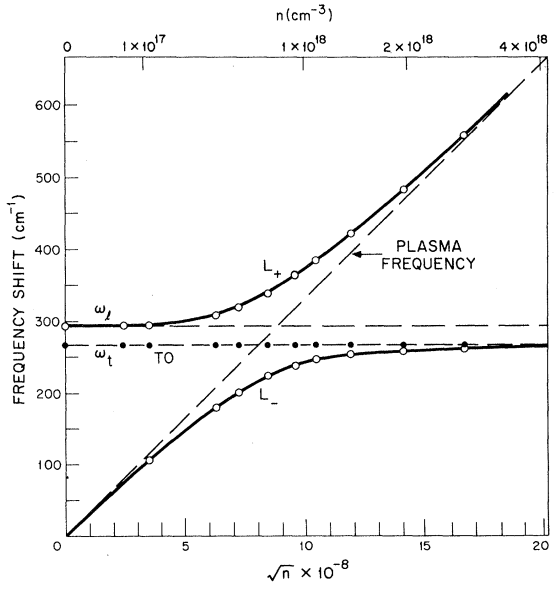


FIG. 1. Frequency shift of the Raman-scattered light in GaAs at room temperature as a function of the square root of the electron concentration. The solid curves labeled $L_+$ and $L_-$ give the frequencies of the mixed longitudinal-phonon–plasmon modes calculated from the roots of the dielectric constant of Eq. (4); the dashed line labeled TO is the transverse optic mode at frequency $\omega_t$.