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# Antiferromagnetism in Chromium Alloys. II. Transport Properties*

A. L. TREGO† AND A. R. MACKINTOSH‡

*Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa*

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The electrical resistivity and thermoelectric power have been studied as a function of temperature in single crystals of Cr containing small concentrations of V, Mn, Mo, W, and Re. The onset of antiferromagnetism is marked by anomalies in the transport properties, and the Néel temperatures can be deduced from these. The variation of $T_N$ upon alloying is qualitatively in accord with the two-band model of Fedders and Martin, especially in its exponentially rapid dependence on electron concentration. In the incommensurable magnetic structures, the most important factors modifying the transport properties are the mutual annihilation of electron and hole regions of the Fermi surface and the consequent reduction in the probability of electron-phonon scattering. Field-cooling experiments in pure Cr indicate that the effect of magnetic superzones is much smaller than these contributions. The electron-phonon scattering depends sensitively on the relation between the energy gap at the Fermi surface and the maximum phonon energy, and consideration of the magnitude of the anomalies in the transport properties below $T_N$, in particular the variation with electron concentration, leads to an approximate value of $2.2k_BT_N$ for the mean energy gap, which is consistent with the theory. In the more concentrated commensurable magnetic structures, on the other hand, superzone effects appear to be dominant, since the change in resistance on ordering is proportional to the ordered moment. When different solutes are added to Cr, the low-temperature thermopower behaves in a very complicated way, but its large magnitude in the more concentrated Cr-Mn alloys can probably be ascribed to magnon drag.

## INTRODUCTION

THE electronic structure and electron-scattering processes in magnetic metals have recently been extensively studied, both experimentally and theoretically. Antiferromagnetic metals are particularly interesting because their electronic structure may be substantially modified by the extra periodicity associated with the magnetic ordering. Thus as an antiferromagnetic metal is cooled through its Néel temperature, the Fermi surface and those properties which depend on it may be significantly altered. It is not possible to study the modification of the Fermi surface at the transition temperature directly because the relatively short mean free path at elevated temperatures precludes the use of the most powerful techniques, but low-temperature studies of pure Cr by the de Haas–van Alphen effect[1] have recently revealed the complexity caused by the magnetic order. Such experiments are not possible with any but the most dilute alloys, however, so we have approached the problem of elucidating the electronic structure of antiferromagnetic Cr alloys by measuring relatively simple transport properties, specifically the electrical resistivity and thermoelectric power.

Anomalies in the transport properties near the Néel temperature of pure Cr have been reported by several workers,[2–5] and a number of measurements on alloys have been reported. Booth[6] measured the electrical resistivity of samples containing up to 25 at. % Re, and deduced the Néel temperatures from the positions of the anomalies. Hamaguchi and Kunitomi[7] and Suzuki[8] have reported extensive measurements of the electrical resistivity of Cr–Mn alloys, while Néel temperatures in Cr–V,[9] Cr–Mo,[10] and Cr–W[11] alloys have been deduced from resistivity anomalies.

The measurements on pure Cr have shown that the details of the temperature dependence of the transport properties are quite sensitive to strain and crystallite size, so that a quantitative investigation requires the use of well-annealed single crystals. In addition, the interpretation of the results requires a detailed knowledge of the magnetic structures, which can only be obtained from neutron-diffraction measurements. Such measurements have been made on polycrystalline samples,[12] and preliminary studies of single crystals by

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† Present address: Los Alamos Scientific Laboratory, Mercury, Nev.

‡ Alfred P. Sloan Research Fellow. Present address: Technical University, Lyngby, Denmark.

[1] B. R. Watts, Phys. Letters **3**, 284 (1963). J. Graebner and J. A. Marcus, J. Appl. Phys. **37**, 1262 (1966).

[2] S. Arajs and G. R. Dunmyre, J. Appl. Phys. **36**, 3555 (1965).

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[6] J. G. Booth, Battelle Memorial Institute Annual Topical Report to Office of Naval Research, 1964 (unpublished).

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[8] T. Suzuki, J. Phys. Soc. Japan **21**, 442 (1966).

[9] M. A. Taylor, J. Less-Common Metals **4**, 476 (1962).

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[11] A. K. Butylenko and V. N. Gridnyev, Ukr. Fiz. Zh. **9**, 325 (1964).

[12] Y. Hamaguchi, E. O. Wollan, and W. C. Koehler, Phys. Rev. **138**, A737 (1965).

TABLE I. Interstitial impurity content of the base chromium (ppm).

| Element | As received | Arc melted | Arc-zone melted |
|---|---|---|---|
| N | 21 | 40 | 30 |
| O | 10 | 22 | 16 |
| C | 57 | 79 | 72 |
| H | 1 | 1 | 1 |

neutron-diffraction and transport measurements have been reported by Møller and the authors.[13] A detailed study of neutron diffraction in powder and single-crystal samples was carried out simultaneously with our transport measurements, and is reported in a separate paper[14] (hereafter referred to as I). The combination of these techniques has allowed us to understand in some detail the relation between the magnetic ordering and the electronic structure and scattering, and has confirmed the general validity of the two-band model of Lomer[15] as extended by Fedders and Martin.[16]

## EXPERIMENTAL PROCEDURE

### Sample Preparation

The single-crystal Cr alloys were grown by an arc-zone melting technique which has been described by Carlson *et al.*[17] Iodide Cr obtained from the Chromalloy Corporation was used as the base metal throughout this investigation. The nominal purities of the materials used were as follows: Cr–99.98%, V–99.2%, Mn–99.99%, Re–99.99%, W–99.9%, Mo–99.9%. In the preparation of the single crystals, the alloys underwent several consolidation arc-melting and arc-zone-melting operations. An analysis of the interstitial impurities in a sample of Cr in its initial state and after arc melting and arc-zone melting is presented in Table I. The specimens were grown in the form of single crystal ingots about $\frac{1}{2}$ in. diam and 6 in. long. In some cases, the ingot consisted of several large grains. Rectangular parallelepipeds of about 2 mm square cross section by 1.5 cm in length were cut from the ingots by a spark erosion cutter. The specimens were then electropolished in orthophosphoric acid and annealed *in vacuo* at 1000°C for 50 h. The compositions of the alloys were determined by chemical analysis. Back-reflection Laue x-ray pictures were taken of all samples to ensure that they were single crystals. The Cr–V, Cr–Mn, and Cr–Re alloy samples had random orientations, while the Cr–W and Cr–Mo alloy samples were prepared with a cube axis perpendicular to all faces of the parallelepiped.

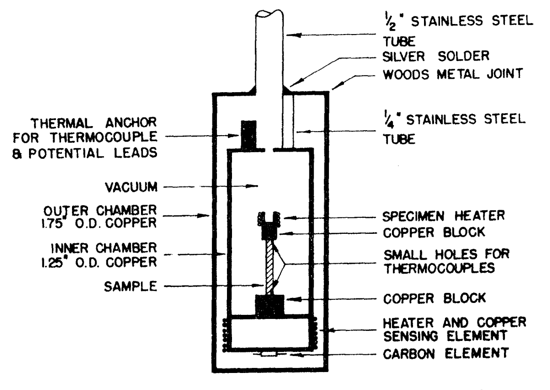

FIG. 1. The sample holder and heat-leak chamber.

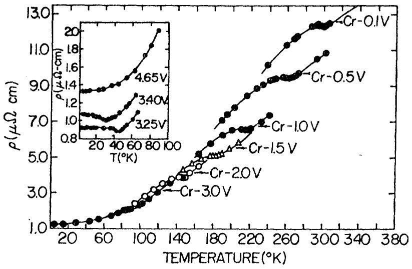

FIG. 2. The electrical resistivity of Cr–V single crystals as a function of temperature.

## APPARATUS

The electrical resistivity was measured with a standard four-lead technique, using razor-blade edges as resistance probes. The sample dimensions were determined with the aid of a travelling microscope. The relative error in these measurements is less than 0.1%, while the absolute error, due to irregularities in the specimen shapes, is about 5%. The thermopower was determined by the method described by Sill and Legvold.[18] The relative error in these measurements is about 0.05 μV/°K as evidenced by the lack of scatter in the data. The absolute error is estimated to be about 5% below 30°K, gradually decreasing to 1% at about 77°K with the limitation that the absolute error is probably never less than 0.1 μV/°K.

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[13] H. B. Møller, A. L. Trego, and A. R. Mackintosh, Solid State Commun. 3, 137 (1965).

[14] W. C. Koehler, R. M. Moon, A. L. Trego, and A. R. Mackintosh, Phys. Rev. **151**, 405 (1966).

[15] W. M. Lomer, Proc. Phys. Soc. (London) **80**, 489 (1962).

[16] P. A. Fedders and P. C. Martin, Phys. Rev. **143**, 245 (1966).

[17] O. N. Carlson, F. A. Schmidt, and W. M. Paulson, Trans. Am. Soc. Metals **57**, 356 (1964).

[18] L. R. Sill and S. Legvold, Phys. Rev. **137**, A1139 (1965).

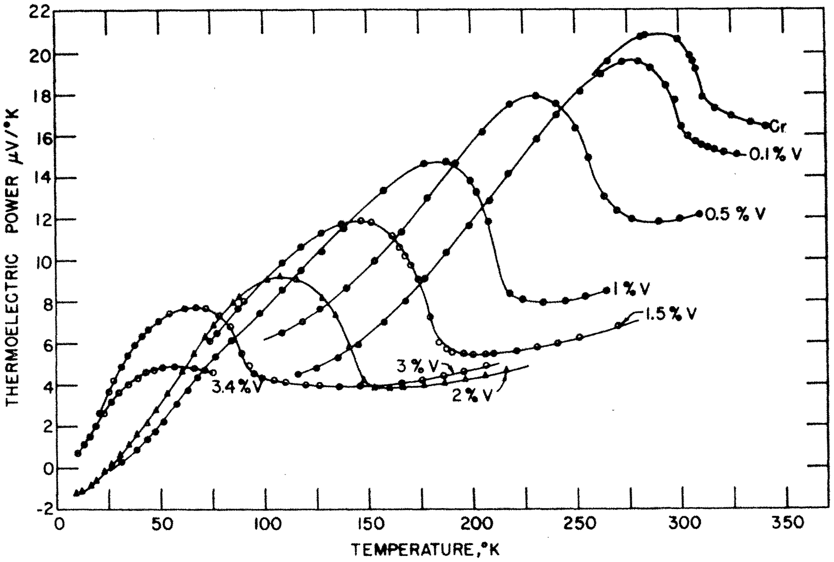

FIG. 3. The thermoelectric power of Cr–V single crystals as a function of temperature.

In order to provide continuously variable temperatures, a heat-leak chamber was used. A schematic diagram of the sample holder and heat-leak chamber is shown in Fig. 1. The sample chamber was connected to the outer chamber by a 1 in. length of stainless-steel tubing. The outer chamber was placed directly in a bath of liquid helium, liquid nitrogen, dry ice and acetone mixture, or ice depending upon the temperature range desired. A standard glass Dewar system was used to hold the cryogenic materials. Any temperature above bath temperature could be obtained by evacuating the chamber and applying Joule heat to a resistance heater glued to the sample chamber. All data were taken under steady-state conditions and generally in the order of increasing temperature. An automatic temperature-control system was incorporated to minimize the time required to achieve steady-state conditions.[19]

Temperature measurements in the range 4.2–25°K were made with Au+0.03% Fe versus Cu thermocouples.[20] Copper versus constantan thermocouples were used for temperatures above 25°K. Thermocouple voltages were measured with a Leeds and Northrup type K-3 potentiometer with a matching electronic galvanometer. The absolute value of the temperature measurements was estimated to be accurate to ±0.2°K below 25°K and to ±0.5°K above 25°K. The thermoelectric and resistance potentials were measured with a Honeywell, Model 2779, low-μV potentiometer with a Sensitive Research photocell galvanometer amplifier as null detector. Voltage changes of 0.01 μV could be measured up to 200 μV.

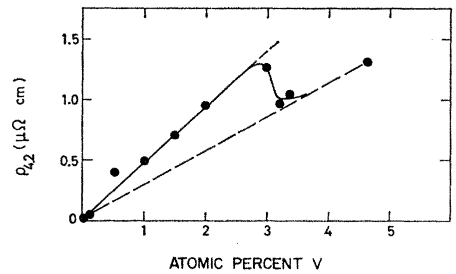

FIG. 4. Residual resistivity as a function of concentration in the V alloys.

For the field-cooling experiments, magnetic fields of up to 25 kG were produced in an electromagnet, while fields of up to 55 kG were obtained in a superconducting solenoid. The samples were cooled through the Néel temperature in the field, and then resistance measurements were performed while the temperature was increased. These experiments were carried out with both longitudinal and transverse field configurations.

## EXPERIMENTAL RESULTS

The electrical resistivity and thermoelectric power in the V alloy system, which was studied in the greatest detail, are shown in Figs. 2 and 3. The Néel temperature falls rapidly with increasing V concentration, and the position of the anomalies in the transport properties shifts accordingly, but the magnitude of the anomalies bears no simple relation to $T_N$ or to the ordered moments. The thermopower is more sensitive to changes in the electronic structure and scattering mechanisms at the antiferromagnetic transition [see Eq. (10)] and consequently generally suffers the greater change, but there is no observable anomaly in $S$ in the 3.4% V sample although the resistivity shows a clear kink. The residual resistivity for these alloys is shown in Fig. 4. It is approximately proportional to the solute concentration in the dilute antiferromagnetic samples,

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[19] Complete details may be found in A. L. Trego, thesis, Iowa State University, 1965 (unpublished).

[20] D. K. Finnemore, J. E. Ostenson, and T. F. Stromberg, U.S. Atomic Energy Commission Report No. IS-1046, 1964 (unpublished).

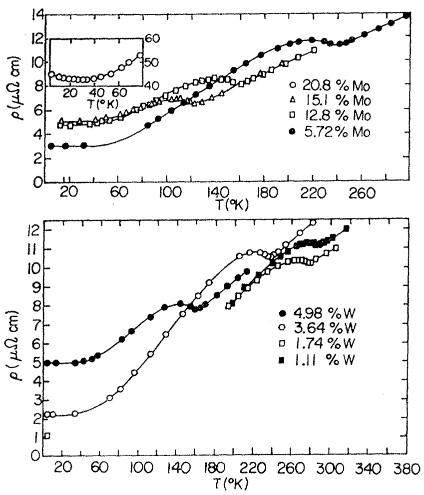

Fig. 5. The electrical resistivity of Cr–Mo and Cr–W single crystals as a function of temperature.

in agreement with Nordheim's rule, but falls rapidly at about 3% V.

The results for Mo and W alloys, shown in Figs. 5 and 6, behave in a qualitatively similar way, except that the low-temperature transport properties of the W alloys appear to be markedly affected by the strong scattering of the electrons by the W impurities. For several compositions in the Cr–W series, two samples, which were prepared completely independently, were used in order to determine the effects of strains and inhomogeneities. As may be seen in Fig. 6, the results depend only on sample concentration, to a good approximation, indicating that the annealing process used was probably satisfactory.

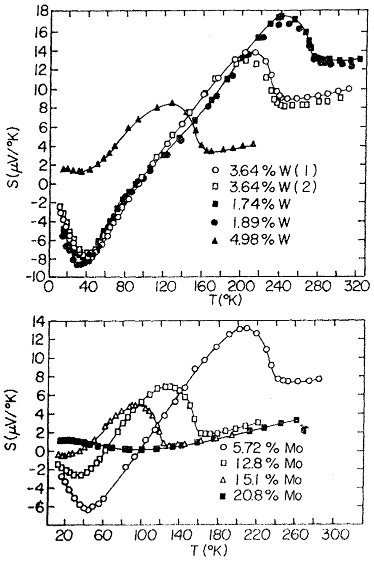

Fig. 6. The thermoelectric power of Cr–Mo and Cr–W single crystals as a function of temperature.

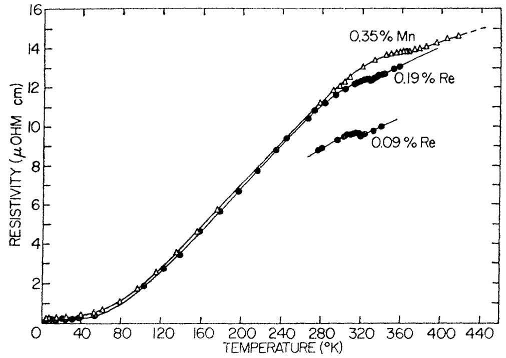

Fig. 7. The electrical resistivity of Cr–Re and Cr–Mn single crystals as a function of temperature.

The Néel temperature rises very rapidly in the Cr–Mn and Cr–Re systems, and it was only possible to make measurements above $T_N$ in very dilute alloys in our apparatus. The resistivity of these dilute samples is shown in Fig. 7, and the thermopower of a number of Mn alloys is shown in Fig. 8. A noteworthy feature is the marked enhancement of the low-temperature hump in the thermopower as the Mn concentration is increased. Further details of the results on these alloys may be found in Ref. 19.

The transition from a commensurable to an incommensurable magnetic structure, which was studied in I, does not produce any noticeable change in the transport properties of the Mn alloys. On the other hand, the 0.8% Re alloy shows a large hysteresis in the thermopower (Fig. 9), which is very similar to that observed in the neutron-diffraction studies,[14] and is presumably due to this transition. No anomalies are observed in the resistivity of this specimen, however, and the spin-flip transition in the very dilute alloys was not manifested by any observable change in the transport properties.

The electrical resistivity as a function of temperature for a single crystal of Cr cooled through its Néel temperature in a magnetic field $H_c$ is shown in Fig. 10. The current direction was along the long [001] axis of the sample while the field was applied along [001] (longitudinal), [100] or [010] (transverse). The electrical resistivity above $T_N$ is independent of field, but on cooling through $T_N$ in a field it falls above or below the

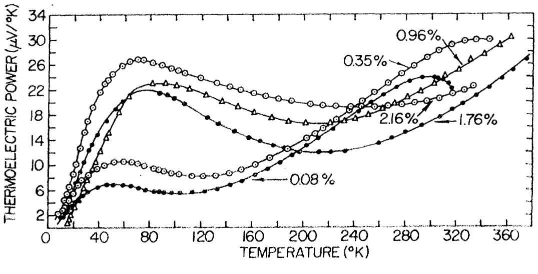

Fig. 8. The thermoelectric power of Cr–Mn single crystals as a function of temperature.

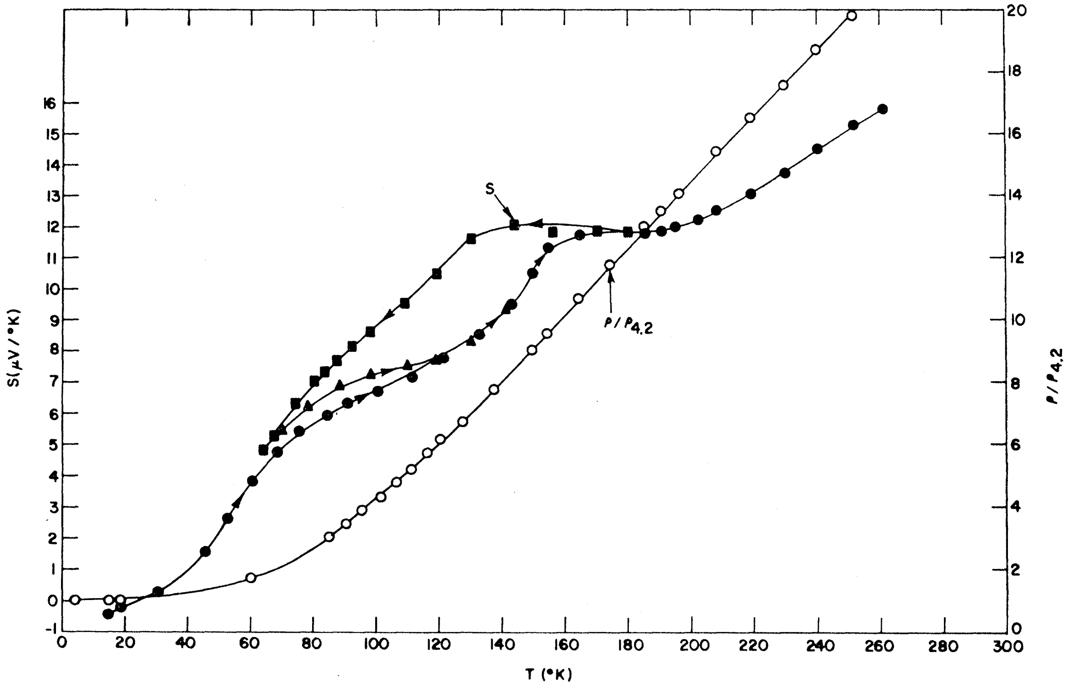

FIG. 9. Resistivity and thermopower of a Cr–0.8% Re alloy. The direction of temperature change is indicated by arrows.

zero field value, depending on whether $H_c$ is longitudinal or transverse. In order to obtain reproducible results, it was necessary to begin each run at about 325°K, and the results for $H_c=0$ could always be reproduced after heating to this temperature. The results for a transverse field are the same for $H_c$ along [010] or [100]. After being cooled in a magnetic field, the crystal retained its anisotropy until warmed above the Néel temperature. The resistance change as a function of temperature, for samples cooled in different longitudinal and transverse fields, and the resistance change at different temperatures, as a function of the cooling field, are shown in Fig. 11. In each case, $\Delta\rho$ is the difference in resistance between the sample cooled through $T_N$ with and without the magnetic field. The normal magnetoresistance in a field of 55 kG was negligible at these temperatures.

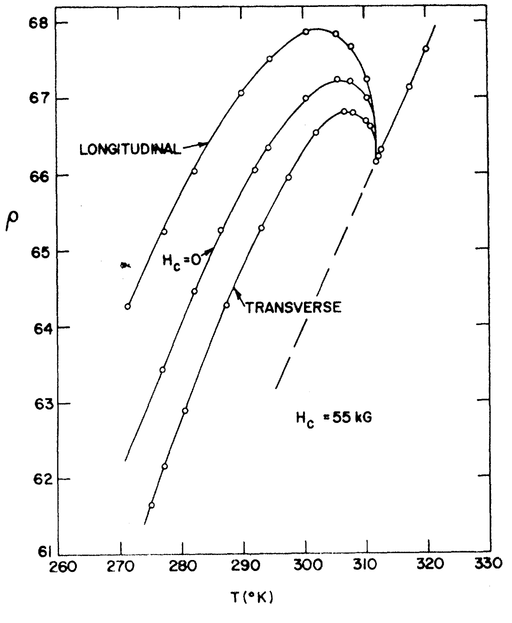

FIG. 10. The electrical resistance of a single crystal of Cr cooled through the Néel temperature in a magnetic field. The current and field were both in ⟨100⟩ directions.

## DISCUSSION

The anomalies in the transport properties provide a convenient means for locating the Néel temperature, and in Fig. 12 we have plotted $T_N$ as a function of concentration for those alloy systems which we studied. These values were generally determined from the position of the discontinuity in slope in the resistivity curves, which gave results in good agreement with the measurements of other authors.[7,11,21] The anomalies in the thermoelectric power were consistent with these values but were somewhat less distinct, probably due to critical scattering of the conduction electrons near the transition. The resistivity anomaly in the 0.35% Mn alloy was very indistinct, as may be seen in Fig. 7, and $T_N$ for this sample was taken from the neutron-diffraction measurements in I.

A qualitative discussion of the change in $T_N$ with

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[21] R. G. Barnes and T. P. Graham, Phys. Rev. Letters 8, 248 (1962).

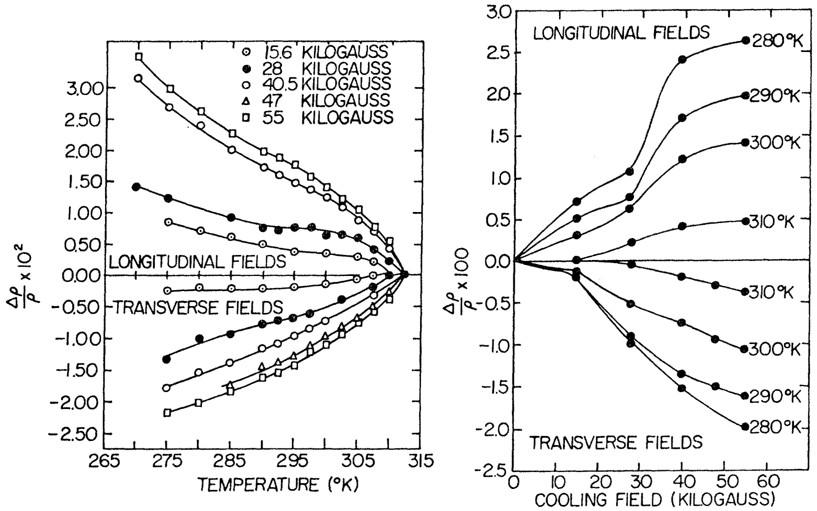

FIG. 11. The relative resistance change as a function of temperature, for different cooling fields, and as a function of cooling field for different temperatures. $\Delta\rho$ is the difference in resistance between the sample cooled through $T_N$ with and without the magnetic field.

solute and concentration was given in I, and we shall now consider in somewhat more detail the variation in the V and Mn alloys, where the $3d$ electronic wave functions are little affected by alloying and the largest effect on $T_N$ is expected to arise from changes in the Fermi surface. Fedders and Martin[16] have analyzed an isotropic model in which two spherical pieces of Fermi surface with radius $k_c$ in different bands are connected by the wave vector $\mathbf{q}$ of the magnetic order. A qualitative account of such a model had previously been given by Muheim and Muller.[22] The Brillouin zone is assumed to be spherical with a Debye radius $K$. For this model, the Néel temperature is given by the equation

$$k_BT_N=1.14\bar{v}[k_c(K-k_c)]^{1/2}f\exp(-1/\lambda), \qquad (1)$$

where $\bar{v}$ is the geometric mean of the Fermi velocities in the two bands and

$$\ln f=(K^2+2Kk_c-6k_c^2)/4k_c^2. \qquad (2)$$

The interaction parameter $\lambda$ is given by

$$\lambda=\gamma^2V(0)k_c^2/2\pi^2v, \qquad (3)$$

where $\gamma$ is a mean overlap matrix element for electrons in the same band, $V(0)$ is the average screened Coulomb potential, and $v$ is the arithmetic mean of the Fermi velocities. If we write

$$\lambda'=\frac{4\gamma^2V(0)k_c^2}{8\pi^2v+\gamma^2V(0)(K^2+2Kk_c-6k_c^2)}, \qquad (4)$$

then Eq. (1) can be expressed as

$$k_BT_N=E\exp(-1/\lambda'), \qquad (5)$$

where $E$ is a typical band structure energy of the order

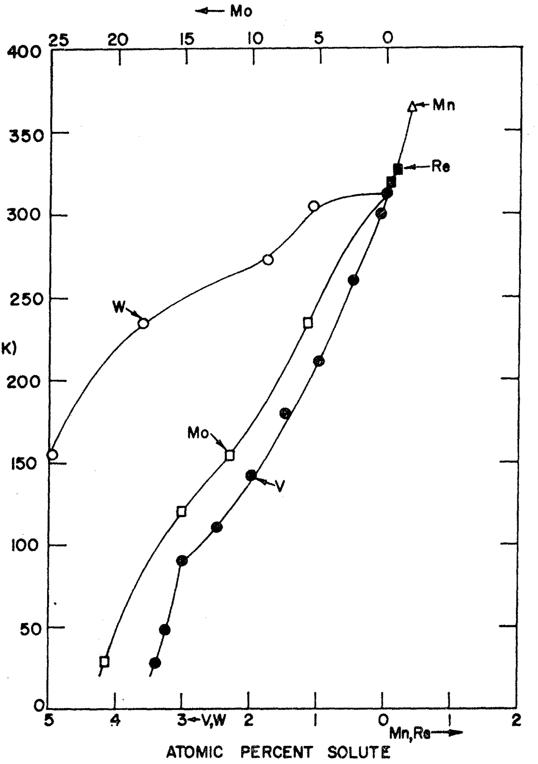

FIG. 12. The Néel temperature as a function of concentration in V, Mn, Mo, W, and Re alloys.

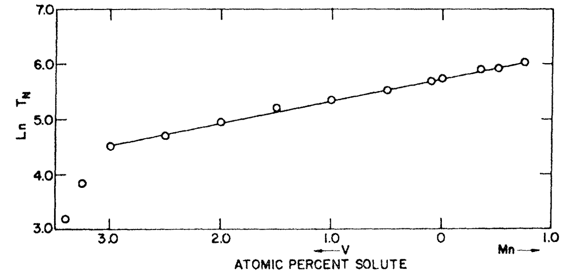

FIG. 13. Ln $T_N$ as a function of electron concentration in V and Mn alloys.

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[22] J. Muheim and J. Müller, Phys. Kondensierten Materie 2, 377 (1964).

of several eV. Since $k_BT_N$ in Cr is about 0.025 eV, $\exp(-1/\lambda')$ is roughly $10^{-2}$, which is comparable in magnitude with the corresponding term in many superconductors. From (5) we have

$$\ln T_N = \ln E/k_B - 1/\lambda', \tag{6}$$

and inspection of Fig. 13 reveals that, neglecting small changes in $E$, $1/\lambda'$ changes almost linearly with electron concentration over the range studied, except that it decreases very rapidly with decreasing electron concentration beyond 3.0% V. We shall see that the transport properties indicate that this is because of a very rapid drop in the area of the electron and hole surfaces connected by $\mathbf{q}$, which is equivalent to a rapid reduction in $k_c$ in the isotropic model.

We now consider the magnitude of the resistance anomalies near $T_N$. If a relaxation time $\tau$ exists, the electrical conductivity tensor is given by

$$\sigma_{ij} = \frac{e^2}{4\pi^3\hbar}\int \tau v_i d\Sigma_j, \tag{7}$$

where $\mathbf{v}$ is the velocity of an electron on a Fermi-surface element $d\Sigma$. The resistivity may therefore be altered on magnetic ordering either by the modification of the Fermi surface by the exchange potential or by a change in the relaxation time. The latter may be written

$$1/\tau = 1/\tau_i + 1/\tau_p + 1/\tau_m, \tag{8}$$

where $\tau_i$ is due to impurity scattering, $\tau_p$ is limited by phonon scattering, and $\tau_m$ represents the effect of magnetic disorder scattering. $\tau_i$ and $\tau_p$ will both be modified if the density of final states is changed. For an intinerant-electron antiferromagnet, magnetic disorder scattering vanishes above $T_N$, where there is no localized moment, and at absolute zero, where ordering is complete. The scattering at intermediate temperatures has not been calculated for a system in which there is a spin-density wave, but it is proportional to the square of the ordered spin and so is rather small in Cr and its alloys as compared with, for instance, the rare-earth metals. We shall not consider, therefore, the magnetic scattering in detail, except to remember that it may cause a small increase in resistivity below $T_N$, especially in those alloys with larger moments.

The electronic wave functions in Cr have predominantly $d$-like symmetry on the hole octahedron and on the body of the electron jack, and the correspondingly flat bands lead to a high density of states but low electron mobility. On the other hand, the mobility on the knobs of the electron jack and on the hole pockets which probably exist at $N$ (see Fig. 14) is relatively high, so that these surfaces make a large contribution to the transport properties, while the high density of final states associated with the $d$ bands will primarily determine the scattering probability.

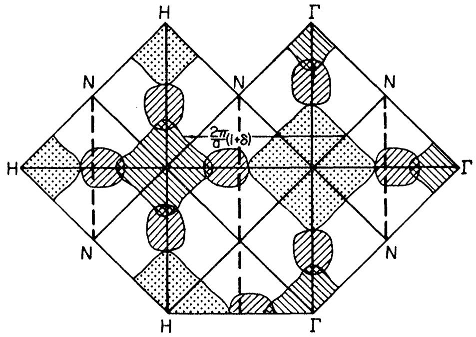

FIG. 14. Section of the Cr Fermi surface in a (100) plane. The dashed lines are magnetic superzone boundaries in the commensurable magnetic structure.

Because the hole octahedron and the electron jack are not generally connected by the $\mathbf{q}$ vector in the commensurable structure found in the more concentrated Mn and Re alloys[23] and do not therefore mutually annihilate in the way discussed in I, the effect of the antiferromagnetic ordering on the transport properties is somewhat different in the commensurable and incommensurable magnetically ordered phases. We shall therefore begin by discussing the resistivity anomalies in those alloys with incommensurable magnetic structures. In Fig. 15, we have plotted the quantity

$$(\rho-\rho_0)/\rho = \Delta\rho/\rho \tag{9}$$

as a function of temperature for these alloys. Here $\rho_0$ is the resistivity in the absence of ordering and may generally be determined by extrapolating the resistivity curve linearly through the Néel temperature. In some cases, $T_N$ occurs in a nonlinear region of the resistance curve in which case the resistivity of a nonmagnetic 4.65% V sample was used to estimate the temperature dependence and hence $\Delta\rho$. The maximum value of $\Delta\rho/\rho$, which we shall call $\Delta$, is shown as a function of electron concentration for V, Mn, and Re alloys in Fig. 16. The largest value of electron concentration corresponds to a 0.35% Mn alloy, which forms a commensurable structure at $T_N$ but is incommensurable at lower temperatures,[14] so that $\Delta$ can be determined quite reliably. It is at first sight surprising that, for concentrations less than about 6.002 electrons/atom, the magnitude of the anomaly increases with decreasing concentration, whereas it was shown in I that the moment decreases rapidly over this range. In the incommensurable alloys, substantial amounts of the electron and hole Fermi surfaces mutually annihilate, and this effect is probably more important than that of the plane superzone boundaries.[14] Both of these effects would by themselves cause a decrease in $\Delta$ with decreasing moment, however, as would the magnetic disorder scattering. The anomalous behavior of $\Delta$ must therefore be explained by the variation of scattering with concentration. At high temperatures, the phonon scattering will predominate, so we shall begin by discussing the effect of the magnetic ordering on $\tau_p$.

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[23] L. M. Falicov and D. R. Penn, Phys. Rev. **158**, 476 (1967).

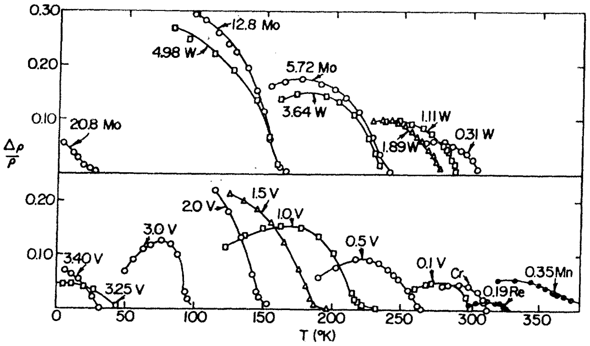

FIG. 15. $\Delta\rho/\rho$ as a function of temperature for V, Mn, Mo, W, and Re alloys.

The partial mutual annihilation of the hole octahedron and the body of the electron jack produces an energy gap $2g$ (see Fig. 8 of I), which can drastically reduce the number of final states into which an electron on the Fermi surface can be scattered by a thermal phonon, and hence can increase $\tau_p$. To estimate the dependence of this effect on the magnitude of the energy gap, we consider a simple model in which the phonons are represented by a Debye spectrum with a sharp cutoff, while the energy gap is assumed constant and the electron and hole surfaces are supposed to be congruent when one is displaced by $\mathbf{q}$. The phonons of higher energy will be much more effective in reducing $\tau_p$ because of both their high density of states and their greater effectiveness in scattering conduction electrons, so that, at a temperature which is not too small compared with the Debye temperature, the energy dependence of $\tau$ will be qualitatively as shown in Fig. 17 for a number of different values of $g$. As is customary in the discussion of transport properties, $\tau(\epsilon)$ is to be interpreted as the relaxation time for electrons at a Fermi energy $\epsilon$ with a density of states appropriate to the true value of $\epsilon_F$. In considering the electrical resistivity, we are interested in $\tau(\epsilon_F)$, and this is plotted as a function of $g$ divided by $\epsilon_p$, the maximum phonon energy, in Fig. 18. $\tau$ is approximately independent of $g/\epsilon_p$ if $g$ is greater than $\epsilon_p$, but there is a sharp discontinuity in slope at $g=\epsilon_p$, below which $\tau$ drops rapidly with $g$.

The electron-diffusion contribution to the thermoelectric power is given by

$$S=\frac{\pi^2k_B{}^2T}{3e}\left(\frac{\partial\ \ln\sigma}{\partial\epsilon}\right)_{\epsilon_F}$$

$$=\frac{\pi^2k_B{}^2T}{3e}\left(\frac{\partial\ \ln\Sigma}{\partial\epsilon}+\frac{\partial\ \ln\bar{l}}{\partial\epsilon}\right)_{\epsilon_F},\qquad(10)$$

where $\Sigma$ is the area of the constant energy surface corresponding to energy $\epsilon$, the mean free path $l=v\tau$, and $\bar{l}$ is an appropriately weighted average. In considering the thermopower, we are therefore interested in $(\partial\tau/\partial\epsilon)_{\epsilon_F}$, and this is shown qualitatively as a function of $g/\epsilon_p$ in Fig. 18(b). The magnetic contribution is negative, thus making a positive contribution to $S$, and in our simple model it falls discontinuously to zero at $g=\epsilon_p$.

We must now consider briefly the effects of departures from this model on the $g$ dependence of $\tau$ and its derivative in real metals. The phonon spectrum of Cr does not follow the Debye spectrum very closely, but it has been measured[24] and has the same general form with a large final maximum and a rather steep cutoff at about 41 meV. It should therefore reproduce the effect of the Debye spectrum fairly closely, except that there might be further discontinuities due to singularities at lower energies. Furthermore, the phonon spectrum is known not to change greatly upon the addition of small amounts of transition metals.[24] The energy gap could vary over the Fermi surface, which would smear out the discontinuities in the density of states and hence in the relaxation time. A similar effect, which is probably more important, is the lack of exact congruence of the electron and hole surfaces when one is displaced by $\mathbf{q}$. This causes the energy gap to be asymmetric about the Fermi level (see Fig. 8 of I), which means that the effective gap for phonon scattering may be locally substantially reduced or increased. This phenomenon will certainly occur to some extent in Cr and may substantially modify the gap dependence of $\tau$. The influence of an effective gap anisotropy of about 20% on the magnetic contribution to $\tau_p$ is shown qualitatively by the dashed curves in Fig. 18.

The relation between these considerations and the experimental results will now be discussed. If the change in the phonon scattering is assumed to have an effect on the resistivity comparable with that of the change in the Fermi surface, the concentration dependence of $\Delta$ can immediately be explained. In pure Cr, then the increase in $\tau_p$ cancels a large part of the increase in resistivity due to the change in electronic structure. As V is added, $g$ falls and, hence $\tau/\tau_0$ also falls. Since the change in electron concentration alters the Néel tem-

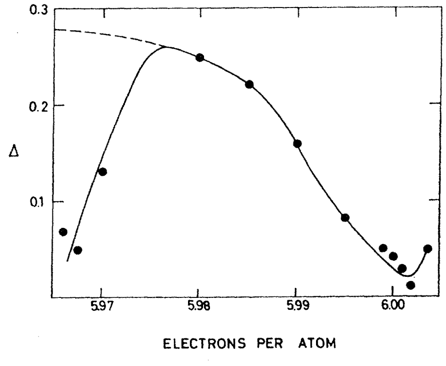

FIG. 16. The maximum value of $\Delta\rho/\rho$ as a function of electron concentration in V, Mn, and Re alloys.

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[24] H. B. Møller and A. R. Mackintosh, in *Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1965); and to be published.

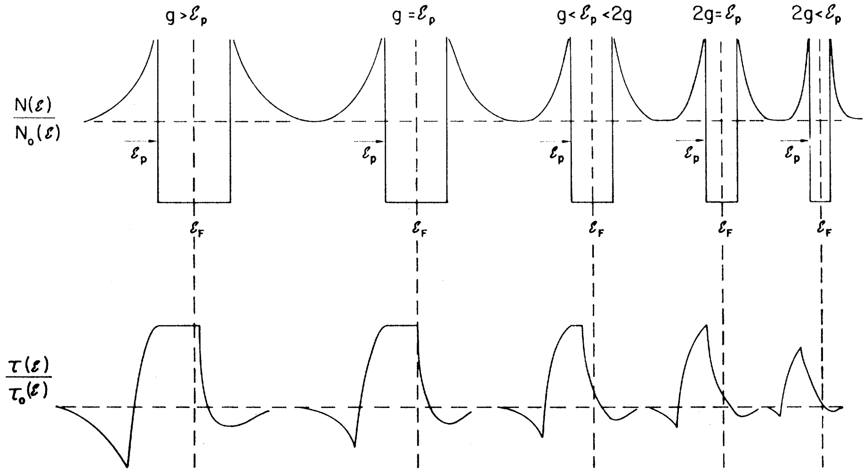

FIG. 17. Schematic variation with energy of the density of states and relaxation time for scattering of electrons by phonons in the incommensurable magnetic structure. $N_0$ and $\tau_0$ are the density of states and relaxation time in the absence of ordering.

perature, the excitation of phonons below $T_N$ also changes, and this is not taken into account in Fig. 18, where a constant phonon excitation is implicitly assumed. This effect will modify the variation of $\tau/\tau_0$ in a way which can be determined only by a detailed theory but will not change the general trend that $\tau$ falls as the gap decreases. Furthermore, the change in impurity scattering becomes relatively important as $T_N$ falls, but again this does not affect the qualitative behavior. We shall show that the change in the area of Fermi surface destroyed due to the decrease in moment is probably small, so that the change in $\tau$ dominates the behavior and the magnitude of $\Delta$ rises rapidly. Conversely, when Re or Mn is added, $\tau/\tau_0$ increases and $\Delta$ falls until the smallest effective gap is equal to $\epsilon_p$, after which $\tau_p$ changes only slowly. The increase in Fermi-surface area destroyed due to the rapidly increasing moment, which is probably principally the result of the increased effect of the superzone planes, then causes a small increase in $\Delta$ until the commensurable structure is reached. We conclude, therefore, that the smallest effective-energy gap in Cr–0.19% Re is equal to the maximum phonon energy of 41 meV, which is $1.5k_BT_N$ for this crystal.

These conclusions are supported by the behavior of the residual resistivity of the V alloys shown in Fig. 4. According to Nordheim's rule, the change in residual resistance should be proportional to the concentration of solute for small concentrations. This relation is approximately satisfied for concentrations as great as 3.0% V, but $\rho_0$ drops sharply beyond this and the nonmagnetcl 4.65% alloy lies on a different line. The higher residuia resistance in the magnetic alloys probably reflects primarily the reduction in the Fermi-surface area consequent on the ordering, which more than cancels the decrease in impurity scattering due to the decreases in the density of states at $\epsilon_F$. The linear variation with concentration probably indicates that neither of these effects changes markedly with concentration up to 3% V, so that the change in residual resistivity is due primarily to the increase in the number of scattering centers. This again shows the extreme sensitivity of the ordering to the area of the surfaces connected by **q** since $T_N$ falls by a factor of about 3 over this region. The very weak antiferromagnetism of the 3.25 and 3.40% V samples is again evident in these results. It appears that the area of the Fermi surface connected by **q** drops very sharply with concentration in this range, and this causes the anomalously rapid decrease in moment[14] and in $T_N$. We believe that this anomalous behavior may be associated with the disappearance of the electron lens at an electron concentration corresponding to 3.0% V and the consequent separation of the body from the knobs

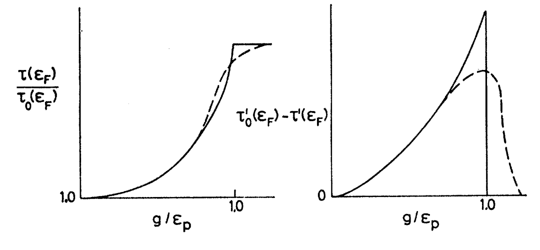

FIG. 18. Schematic variation of $\tau$ and its derivative with the ratio of the half-gap to the maximum phonon energy. The full line represents the simple model, and the dashed line takes into account an effective gap anisotropy of about 20%.

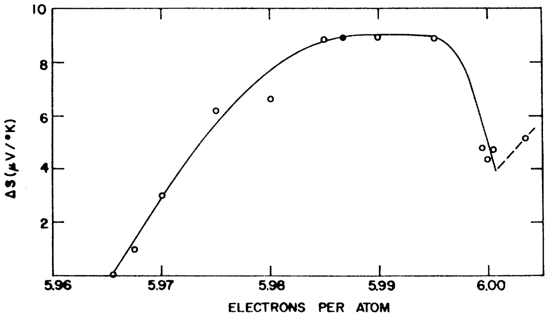

FIG. 19. $\Delta S$ as a function of electron concentration in V, Mn, and Re alloys.

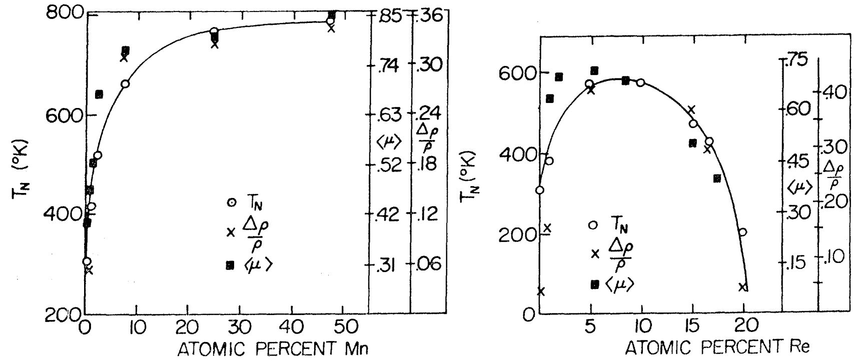

FIG. 20. $\Delta\rho/\rho$ at complete ordering, the Néel temperature, and the ordered moment against concentration in Mn and Re alloys.

of the electron jack (see Fig. 7 of I). This would cause a sudden rounding of the body, which would then be parallel to the hole octahedron over only a small area.

In order to obtain an estimate of the mean gap, we consider the anomalies in the thermopower. At high temperatures the diffusion term in the paramagnetic phase is linear in $T$, and it is therefore possible to determine the contribution of the magnetic ordering to $S$. For those alloys which order at lower temperatures, this separation can be carried out approximately by comparison with the nonmagnetic 4.65% V alloy. A plot of $\Delta S$, the maximum value of the magnetic contribution against electron concentration, is shown in Fig. 19. It is again necessary to invoke the change in phonon scattering to explain the dependence of $S$ on magnetic moment. The change in electronic structure on magnetic ordering will affect the thermopower in a complicated way. Magnetic superzones which cut the Fermi surface generally increase its magnitude,[18] while electron-hole annihilation might be expected to reduce it. On the other hand, the change in phonon scattering will produce a positive contribution, and this apparently predominates in the dilute V alloys. It is interesting that the two affects seem to cancel in the 3.4% V alloy, so that no thermopower anomaly is observed at $T_N$. From Figs. 18 and 19, it appears that the mean gap is approximately equal to the maximum phonon energy of 41 meV in the 1.0% V sample and that there is a considerable spread in the effective gap energy. From the value of the Néel temperature, we therefore have

$$g_0 = 2.2 k_B T_N(\text{expt}). \qquad (11)$$

It was originally suggested by Overhauser[25] that the superzone energy gaps in Cr should be of order $k_B T_N$, and from their analysis of the Lomer model, Fedders and Martin[16] derived the value

$$g_0 = 1.76(v/\bar{v}) k_B T_N(\text{theor}). \qquad (12)$$

Since $v$ must be greater than or equal to $\bar{v}$, the agreement between theory and experiment is reasonable. The dependence of $\Delta S$ on concentration indicates that there is a wide range of effective-gap energies, so that there is an almost uniform distribution of effective gaps in the range 1.8–2.5$k_B T_N$, while, as concluded from the resistivity measurements, effective gaps as small as 1.5$k_B T_N$ probably exist. As emphasized earlier, this need not imply an anisotropy of band splittings of this magnitude but may simply reflect the fact that the splitting does not occur precisely at the Fermi level in some regions of **k** space.

The use of the phonon spectrum as a caliper for the energy gap suffers from the disadvantage of being rather an indirect method, so that a considerable amount of interpretation is required. In this connection it would be valuable to carry out numerical calculations of the temperature dependence of the transport properties taking into account possible effective gap anisotropy, the temperature dependence of the gap, and the excitation of phonons, and using a realistic phonon density of states. It would also clearly be of interest to attempt a measurement of $g_0$ by more direct means such as optical absorption or electron tunneling, but these experiments are unlikely to be so informative as in a superconductor.[16,26] Thermal excitation across the energy gap should give an exponential contribution to the heat capacity, but this term would be difficult to isolate from the other contributions.

The transport properties of the Mo and W alloys can be accounted for by similar considerations. As may be seen in Fig. 15, the resistivity anomalies behave very similarly to those in the V alloys, and, to a fair approximation, their magnitudes depend only on the Néel temperatures, as expected. The thermopower anomalies also behave similarly to those in the V alloys. The low-temperature properties are, however, very different from those of the V alloys because the electrons are scattered more strongly by the Mo and W impurities than by V and because the phonon spectrum is also modified by the heavy impurities, which especially affect the thermopower.

The preceding discussion requires modification before it can be applied to the simple commensurable antiferromagnetic structure, because the **q** vector of the magnetic ordering does not then generally connect

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[25] A. W. Overhauser, Phys. Rev. **128**, 1437 (1962).

[26] W. A. Harrison, Phys. Rev. **123**, 85 (1961).

large areas of electron and hole Fermi surface. This means that there is little mutual annihilation of such surfaces on magnetic ordering so that the states near the Fermi energy are relatively little affected and the scattering probabilities are not greatly changed. In such a situation, we should expect that the predominate effect on the resistivity is due to plane superzone boundaries. Miwa[27] and Elliott and Wedgwood[28] have shown that a superzone plane which cuts the Fermi surface, as depicted for instance in Fig. 14, causes a resistance change $\Delta\rho/\rho$ which is proportional to the ordered moment. In Fig. 20 we have plotted the value of $\Delta\rho/\rho$ at a temperature corresponding to complete ordering, the Néel temperature,[6–8] and the ordered moment[14] against concentration in the Cr–Mn and Cr–Re systems. For the more concentrated alloys, the relative resistance change is approximately proportional to the moment, as expected. For the more dilute alloys, however, the situation is more complicated. Then the **q** vector is not far from the separation between the octahedral faces of the electron and hole Fermi surfaces, so that many states near $\epsilon_F$ are still affected and the phonon scattering is somewhat reduced. Since this effect and the precise way in which the Fermi surface itself is affected by the ordering both vary in a complex manner as the number of conduction electrons is increased, the description of the transport properties in these alloys will require a detailed model.

Experiments on the de Haas–van Alphen effect[1] have made it clear that the magnetic structure of Cr is tetragonal. Neutron-diffraction[29] studies show that this structure consists of a single spin-density wave which is distributed in domains randomly among the three ⟨100⟩ directions in an untreated crystal and tends to orient itself with **q** along the direction of a magnetic field applied in a [100] direction. The existence of only a single spin-density wave would be anticipated on the basis of the Lomer-two-band mechanism since the lowering of energy is primarily accomplished by the mutual annihilation of the octahedral portions of the Fermi surface and this process is completed by a single wave. On the other hand, if the antiferromagnetism were due to a mechanism of the type suggested by Overhauser,[25] we might expect a further energy lowering by the formation of waves along the other ⟨100⟩ directions.

Cooling through the Néel temperature with a magnetic field along [100] therefore alters the domain population in such a way that **q** vectors along the field predominate, and the evidence from neutron-diffraction measurements[29] is that this process generally saturated before fields of 55 kG, so that all **q** vectors point in the direction of the field. This conclusion seems to be supported by our experiments. As we have seen, the resistance is altered by the magnetic ordering through a number of mechanisms, and of these only the formation of magnetic superzone planes in the direction of **q** should lead to a significant anisotropy in the resistivity. The annihilation of the electron and hole surfaces occurs primarily at octahedral faces and both the consequent reduction in Fermi-surface area and the change in phonon and impurity scattering affect the resistance almost isotropically. The magnetic disorder scattering could be anisotropic, but it is probably small in Cr, and its anisotropy is therefore negligible. We therefore ascribe the increase in resistivity due to cooling in a field along the current direction to a reorientation of the superzones in the crystal. Since superzones normal to the current direction should have a negligible effect on the resistivity,[28] the difference between the resistivity for longitudinal and transverse field cooling gives the effect of superzones on the resistivity in the direction of **q** in a single domain, which is to give a $\Delta\rho/\rho$ in pure Cr of about 0.015 at complete ordering. We can separate the effect of the change in phonon scattering from the combined effects of electron-hole Fermi-surface annihilation and impurity scattering by considering the residual resistivity results of Fig. 4. The latter two together give a $\Delta\rho/\rho$ of about 0.35 while, from Fig. 10, the decrease of electron-phonon scattering cancels all except about 0.02 of this in pure Cr and therefore gives $\Delta\rho/\rho$ of about $-0.33$ at complete ordering. These figures indicate that a substantial proportion of the octahedral surfaces are destroyed on ordering, especially as the most mobile electrons are little affected. This is in agreement with the results of low-temperature specific-heat measurements.[10,22]

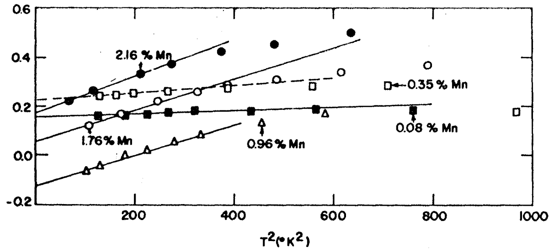

FIG. 21. $S/T$ as a function of $T^2$ in the Mn alloys.

Finally, we consider briefly some features of the low-temperature thermopower of our samples. In addition to the diffusion term of Eq. (10), there may be a contribution due to the dragging of electrons by collisions with phonons or, in magnetic metals, with magnons. The dispersion relations for magnons in spin-density-wave systems are predicted to be linear at small wave vectors,[16] so that we expect the same temperature dependence for both phonon and magnon drag.[30] The latter will be small in V alloys, where the ordered moment is small, but might be expected to grow rapidly

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[27] H. Miwa, Progr. Theoret. Phys. (Kyoto) **28**, 208 (1962).

[28] R. J. Elliott and F. A. Wedgwood, Proc. Phys. Soc. (London) **81**, 846 (1963).

[29] A. Arrott, S. A. Werner, and A. Kendrick, Phys. Rev. Letters **14**, 1022 (1965); T. J. Bastow and R. Street, Phys. Rev. **141**, 510 (1966).

[30] M. Bailyn, Phys. Rev. **126**, 2040 (1962).

TABLE II. Values of $a$ and $b$ coefficients for Cr–Mn alloys.

| % Mn | $a[\mu V/(°K)^2]$ | $b[10^{-4}\mu V/(°K)^4]$ |
|---|---|---|
| 0.08 | 0.14 | 1.3 |
| 0.35 | 0.23 | 1.4 |
| 0.96 | −0.13 | 6.5 |
| 1.76 | 0.055 | 6.4 |
| 2.16 | 0.17 | 7.5 |

with the moment on the addition of Mn. We therefore interpret the large low-temperature thermopower in the commensurable Cr–Mn alloys as a manifestation of magnon drag. In the presence of phonon or magnon drag, the low-temperature thermopower can be written in the form

$$S=aT+bT^3, \tag{13}$$

so that $S/T$ should vary linearly with $T^2$. Such a plot is shown in Fig. 21, and Table II gives the values of $a$ and $b$ derived from it.

The effect of the increased moment and the transition to a commensurable magnetic structure are apparent in both the diffusion and drag terms. The former has a tendency to increase with increasing moment, combined with a sharp drop at the commensurable transition, while the latter increases sharply at the transition.

The phonon-drag contribution changes very little with the addition of V and is approximately the same in a 4.65% V crystal as in pure Cr. This is consistent with the small scattering of phonons in Cr by V, which has a very similar mass. On the other hand, a small concentration of Mo or W, which have much greater masses, causes the low-temperature hump to become negative, and it decreases in size with increasing concentration. The latter effect is probably due to the decrease in phonon free path caused by the strong phonon scattering from the heavy impurities. The thermopower has been observed to behave unpredictably on the addition of small amounts of impurities in other systems,[31,32] and this behavior has been attributed to changes in the anisotropy of impurity and phonon scattering. Since the principal difference between W and V in Cr lies in the behavior as an electron or phonon-scattering center, it is likely that this is also the mechanism in this case, but a detailed explanation is not possible without further experimental and theoretical work. The difference in phonon scattering between Re and Mn in Cr must presumably also be the reason why the hysteresis in the commensurable-incommensurable transition is evident in the thermopower of alloys of the former but not the latter. This puzzling feature serves to emphasize the complexity of the interactions between electrons, phonons, and magnons in the presence of thermal and electrical gradients in these systems.

We have found, therefore, that a careful study of the transport properties yields a considerable amount of information about Cr and its antiferromagnetic alloys. The Néel temperature can be determined from the position of the anomalies in the transport properties, and we conclude that the variation of $T_N$ on alloying is qualitatively in accord with the predictions of the two-band model, especially in the exponentially rapid dependence on electron concentration. In the incommensurable structures, the most important factors modifying the transport properties are the mutual annihilation of the electron and hole regions of Fermi surface and the consequent reduction in the probability of electron-phonon scattering. Field-cooling experiments on pure Cr indicate that superzone effects are much smaller than these contributions. The electron-phonon scattering depends sensitively on the relation between the energy gap and the maximum phonon energy, and consideration of the magnitude of the anomalies in the transport properties below $T_N$, in particular the variation with electron concentration, leads to a value of the energy gap close to that predicted by Fedders and Martin.[16] In the more concentrated commensurable structures, on the other hand, superzone effects seem to be dominate since the change in electrical resistance is proportional to the ordered moment. The low-temperature thermopower behaves in a very complicated way when different solutes are added to Cr, but its large magnitude in more concentrated Cr–Mn crystals can probably be ascribed to magnon drag.

No very detailed analysis of the temperature dependence of the transport properties below the Néel temperature has been given in this paper, although it has been possible to interpret certain gross features in a fairly satisfactory way. A more thorough discussion must await the detailed theoretical analysis of the effect of a spin-density wave on the transport properties of a two-band system, and we hope that such an analysis will soon be forthcoming.

## ACKNOWLEDGMENTS

The experiments described in this paper would not have been possible without the generous cooperation of F. A. Schmidt, who used his great skill to provide us with the large variety of single crystals used. We have enjoyed many illuminating discussions with Professor T. L. Loucks, who provided us with unpublished information about the band structure of chromium. Discussions with Dr. D. Penn, Professor L. M. Falicov, Dr. W. C. Koehler, and Dr. R. M. Moon are also gratefully acknowledged. One of us (ALT) was supported by an Atomic Energy Commission Postdoctoral Fellowship during part of this study.

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[31] D. Greig and J. P. Harrison, Phil. Mag. **12**, 71 (1965).

[32] C. Van Baarle, Physica **33**, 424 (1967).