PHYSICAL REVIEW B VOLUME 1, NUMBER 4 15 FEBRUARY 1970

Lorenz Number of Chromium

J. F. Goff
U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland 20910

(Received 15 September 1969)

The thermal and electrical conductivities κ and σ, respectively, have been measured for chromium between approximately 1.5 and 330°K in order to determine the Lorenz number $L=\kappa/\sigma T$. Since at 330°K these data agree with the higher-temperature measurements by Powell and Tye, an analysis has been developed to encompass both sets of data. Although L shows the usual metallic behavior at low temperatures, at all temperatures above 90°K it is greater than the expected Sommerfeld value ($L_0=2.445\times10^{-8}$ V^2/deg^2). It is not possible to account for this anomaly by the usual assumption of a lattice component of thermal conductivity without allowing the component itself to become anomalous. Klemens has pointed out that anomalous values of L are expected in transition metals at high temperatures because the Fermi skin begins to encompass their complicated band structure. Analysis of L(Cr) in these terms shows that the transport coefficients can be separated into two factors: one which has the temperature dependence of single definite scattering processes above and below the Néel temperature, and another which is the integral of a quantity that has the characteristics of the known band structure. Since this integral is temperature-dependent, it is possible to state that certain anomalies in the transport properties of chromium are due to its band structure. It appears that above the Neél temperature Cr may be approaching nondegeneracy.

I. INTRODUCTION

SOME time ago, Powell and Tye[1] found that the measured Lorenz number L of chromium was greater than the Sommerfeld value ($L_0=2.445\times10^{-8}$ V^2/deg^2) (Ref. 2) over the temperature range from about 323 to 1300°K. More recently, Goff[3] and Moore and co-workers[4] determined that L became larger than L_0 near 90°K and so remained up to the Néel temperature ($T_n=313$°K) (Ref. 5) where there seemed to be further anomalies. Finally, it is possible to construct L from the early low-temperature measurements of Harper and co-workers[6] and so show that their data also indicate the beginning of anomalously large values.

The usual assumption is that whenever $\Delta L=L-L_0>0$ the electronic thermal conductivity κ_e has been increased by a lattice component κ_g. However, Powell and Tye concluded that this κ_g would itself have to be anomalously large; and the value suggested by Moore did not reduce L to L_0. Later in the discussion it is seen that because κ_e and κ_g have different temperature dependences, it is not possible to explain the anomalous ΔL without κ_g itself behaving anomalously in some temperature range. Thus, one would like another explanation.

Recently, Klemens[7] pointed out that L_0 is a consequence not only of equivalent elastic relaxation times for the electrical and thermal-conduction processes, but also of the small energy dependence of the density of states and scattering processes within a few KT of the Fermi surface of a metal (the Fermi skin). Since the band structure of transition metals is more complex, one would expect these two quantities to show increasingly complicated energy dependences within the Fermi skin as the temperature is raised; there will be a change from metallic to semimetallic behavior with concomitant anomalies in L with increasing temperature. Klemens has called the formulation of these ideas the method of moments.[7]

It is the purpose of this paper to show that when L(Cr) is analyzed in this way, the data themselves suggest a physically reasonable electronic model of the conduction processes that produce the anomaly. It proves possible to factor the transport coefficients into two terms. The first, being temperature-dependent over the whole temperature range, is indicative of the scattering processes and band-structure properties at the Fermi level. The second, although temperature-dependent also, is the integral of a quantity that has the characteristics of the known band structure; it has a minimum at the Fermi level, is symmetrical about it, and is temperature-dependent only over a small range of temperature just below T_n. As a result of this second factor, the transport properties of chromium are anomalous to the highest temperatures measured; the paramagnetic metal is not normal.

The present measurements have been made on a polycrystalline sample. After the first anneal, the temperature range from about 1.5 to 230°K was covered; after the second anneal the range was extended to 330°K. Since the analysis uses the data of Powell and Tye in addition, there is an extensive comparison in the discussion of the data of the transport property measurements extant.

II. EXPERIMENTAL

Apparatus

The calorimeter shown in Fig. 1 is surrounded by a liquid refrigerant held in the usual double Dewar

---

[1] R. W. Powell and R. P. Tye, J. Instr. Metals **85**, 185 (1956).
[2] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960).
[3] J. F. Goff, *Proceedings of the Seventh Conference on Thermal Conductivity* (Natl. Bur. Std. Special Publication No. 302, Washington, D. C., 1968), p. 311.
[4] J. P. Moore, R. K. Williams, and D. L. McElroy, Ref. 3, p. 297.
[5] S. Arajs and G. R. Dunmyre, J. Appl. Phys. **36**, 3555 (1965).
[6] A. F. A. Harper, W. R. G. Kemp, P. G. Klemens, R. J. Tainsh, and G. K. White, Phil. Mag. **2**, 577 (1957).
[7] P. G. Klemens, in *Thermal Conductivity*, edited by R. P. Tye (Academic Press Inc., New York, 1969), Vol. 1, p. 1.

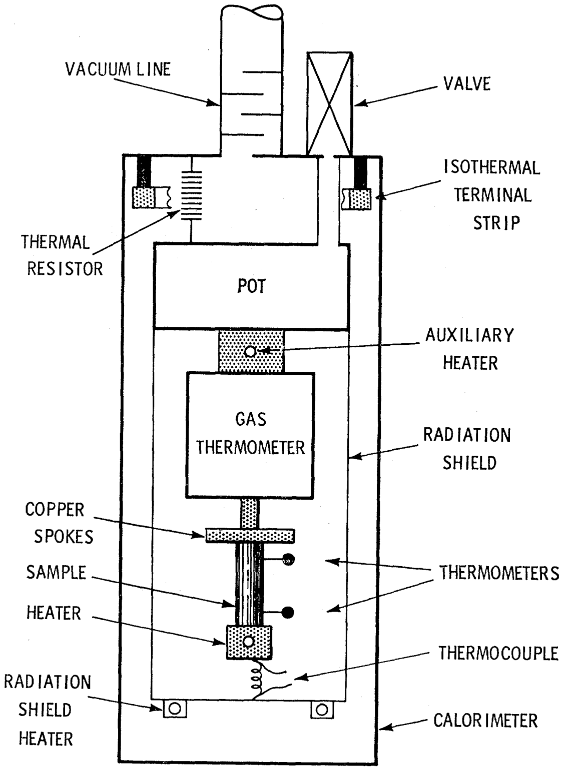

FIG. 1. Schematic of the calorimeter. It is held in the usual double Dewar system.

system. It was designed to measure the thermal conductivity by the steady heat flow method.[8] By using the thermometer contacts as potential probes it is possible to measure the thermoelectric power and the electrical resistivity in the same experiment. The electrical resistivity is measured during an isothermal portion of the experiment with reversal of current to minimize stray emf's. The various thermometers are usually calibrated during this portion of the experiment. All sample connections are pressure contacts.

The sample-gas thermometer-pot assembly is connected to the refrigerating bath through either the thermal resistor (a light copper wire) or directly by opening the valve so that the refrigerant can fill the pot. With the pot empty it is possible to heat the assembly above the temperatures obtainable with liquid He or liquid N_2 so that measurements can be made. Alternatively, with the pot full it is possible to measure at the temperature of the refrigerant, which can be varied by pumping on it. In this way, measurements can be made in a temperature range from about 1.3 to 330°K. Measurements can also be made by allowing the apparatus to drift up in temperature slowly.

The various heaters are $\frac{1}{2}$-W thin-film glass-core resistors which are inserted into copper and sealed with glyptol enamel. There is no need to prepare them in any way. The sample heater is about 2000 Ω so that it can be used at low current to minimize lead heating. All heaters are dc.

Heat leaks are minimized by evacuating the sample chamber to less than 10^{-5} Torr, enclosing the sample in a guarded copper radiation shield, and minimizing the temperature gradients across electrical connections. The shield is guarded by heating with the shield heaters until the thermocouple between it and the sample heater indicates less than a degree difference in temperature. It is also packed with asbestos fiber to prevent coaxial heat transfer by radiation. The electrical leads are 2-m lengths of No. 40 copper wire fashioned into free-formed coils which are thermally connected to the sample base by wrapping the free end about the copper spokes and securing with GE 7031 varnish. These free ends are then connected to the isothermal terminal strip, which is at the temperature of the calorimeter top. It is estimated that the error due to stray heat leaks is less than the scatter in the data.

Different thermometers are used to measure the temperature difference $\Delta T = T_1 - T_2$ in the various temperature ranges. Below 77°K, it is measured by two 100-Ω $\frac{1}{10}$-W Allen-Bradley carbon resistors. At higher temperatures it can be measured either by a differential thermocouple made of 0.13-mm Au-2.11 at.% Co: Manganin wire coiled and fastened as described above or by two platinum resistors. The thermocouple is electrically insulated from the copper thermometer blocks by cigarette paper and glyptol enamel. The platinum resistors are encased in copper shields with the leads thermally anchored to the case. In the temperature range crucial to this paper (100 to 200°K), the data taken with these two types of thermometers agree to within 2%. At the highest temperatures it was necessary to use the platinum resistors exclusively because the thermoelectric power of the thermocouple behaves anomalously.

The carbon resistors are calibrated against the temperature of the gas refrigerants at 4.2 and 77°K. At intermediate temperatures they are assumed to obey a modified Clement-Quinnell formula.[9] Below 4°K, where they can be compared with the vapor-pressure temperature scale of liquid He, this calibration is found to yield deviations between the two thermometers of about 1 mdeg. A comparison of these thermometers with the gas thermometer above 77°K indicates that the linear Clement-Quinnell plot extends to about 120°K for carbon resistors of this denomination. The differential thermocouple is calibrated during each experiment for subsequent use by connecting it between cells in the gas thermometer and the isothermal terminal strip. The platinum resistors are supplied by a nominal calibration in terms of their reduced resistances (Rosemont

---

[8] N. Pearlman, *Methods of Experimental Physics* (Academic Press Inc., New York, 1959), Vol. 6A, p. 385.

[9] J. R. Clement, *Temperature—Its Measurement and Control in Science and Industry* (Rheinhold Publication Corp., New York, 1955), Vol. II, p. 382.

TABLE I. Sample parameters.

Sample	Preparation	Anneal	$\rho_0(\Omega\ \text{cm})$	$\rho(300°\text{K})/\rho(4°\text{K})$
Goff: Cr(1)	arc-cast	24 h at 900°C	1.834×10^{-7}	72
Cr(2)	arc-cast	24 h at 900°C	1.45×10^{-7}	88
Powell and Tye	electro-deposited	1410°C	5×10^{-8}	270
Arajs and Dunmyre	arc-cast	···	8.11×10^{-8}	160
Harper *et al.*				
No. 2	forged	partial	1.81×10^{-7}	≈ 68
No. 3	forged	partially recrystalized	1.25×10^{-7}	≈ 98
No. 5	forged	fully recrystalized	5.5×10^{-8}	≈223

Engineering, Minneapolis, Minn). In order that the platinum resistance calibration would be independent of the other calibrations, their temperature scale has been composed of the average temperature of four such nominally calibrated resistors. As pointed out above, this scale gave results compatible with the gas thermometer calibration of the thermocouple.

Details of the gas thermometer are given elsewhere.[10] Corrections are made for the dead volumes, the second virial coefficient of He, and the thermal expansion of the thermometer bulb. It has a discrimination of about 0.01°K and is accurate to about 0.2°K.

Electrical potentials are measured by a Leeds and Northrup K3 potentiometer or a Hallmark-Lindeck source with a photocell galvanometer amplifier. Stray emf's are less than 0.5 μV. The data from the portions of the experiment using liquid He and liquid N_2 join well together as long as steady-state conditions are maintained. The estimated error depends upon the temperature range but is no more than about 5% for the thermal conductivity and 1% for the electrical resistivity. The least accurate range is between about 60 and 77°K.

III. SAMPLE

The sample was ground to size from a polycrystalline ingot which was cast in an oxygen-free copper boat by melting electrolytic Cr with an argon arc. The final dimensions were about 4×4×50 mm, with about 35 mm between thermometer contacts.

The starting material was analyzed as follows (wt.%): Cr: 99.92%; Mn: 0.004%, Fe: 0.005%, Mg: 0.002%, Cu: 0.003%, and the balance S, P, and Ni.

The sample was annealed twice in a vacuum at 900°C for 24 h. These samples will be called Cr(1) and Cr(2), respectively. Significant parameters are given in Table I.

IV. DATA

A. Electrical Resistivity

Although there have been many measurements of the electrical resistivity ρ of Cr in the vicinity of T_n, very few extend over a large enough temperature range so that it is possible to extract the ideal resistivity ρ_i from the data. Consequently, the following discussion of the data shown in Fig. 2 can be only suggestive.

ρ(Cr) is not simple. Not only does it seem to depend upon the way in which the sample was prepared but the preparation seems to affect it more in the neighborhood of T_n and above than it does at lower temperatures.[11] The data shown in the figure fall into two groups: samples prepared in an isotropic manner (arc-cast or electro-deposited) and the single sample prepared in a directional manner (hot-extruded or forged). The data for these two types differ down to rather low temperatures. The method of preparation and principal parameters of the samples shown in Fig. 2 are given in Table I.

Below T_n the solid lines shown in the figure were derived from the data of Arajs and Dunmyre.[5] By assuming Matthiessen's rule (2)

$$\rho=\rho_0+\rho_i, \tag{4.1}$$

where ρ_0 is the residual resistivity, it was possible to extract ρ_i from their data and then to recombine it with the ρ_0's of the present experiment. The fact that the data of this experiment agree with the solid line within experimental accuracy implies that Matthiessen's rule is obeyed up to temperatures near T_n for samples prepared in the same manner. Thus, while the single point obtained by Powell and Tye[1] in this lower-temperature range agrees very well with these data, the ρ_i (sample No. 5) data of Harper and co-workers[6] who measured a forged sample are somewhat lower in magnitude and show a lesser temperature dependence at the lowest temperatures. At temperatures near T_n, Powell and Tye's data are somewhat greater than those of the other samples. The reason for this difference is not known but may be the result of an incomplete anneal of the electro-deposited Cr.

The annealing experiments of Powell and Tye[1] on electro-deposited Cr and those of Sabine and Svenson[12] on hot-extruded Cr show that ρ decreases when annealed, although at least one experiment by Powell and

---

[10] J. F. Goff, Ph.D. thesis, Purdue University, 1962 (unpublished).

[11] M. J. Marcinkowski and H. A. Lipsitt, J. Appl. Phys. **32**, 1238 (1961).

[12] T. M. Sabine and A. C. Svenson, Phys. Letters **28A**, 443 (1968).

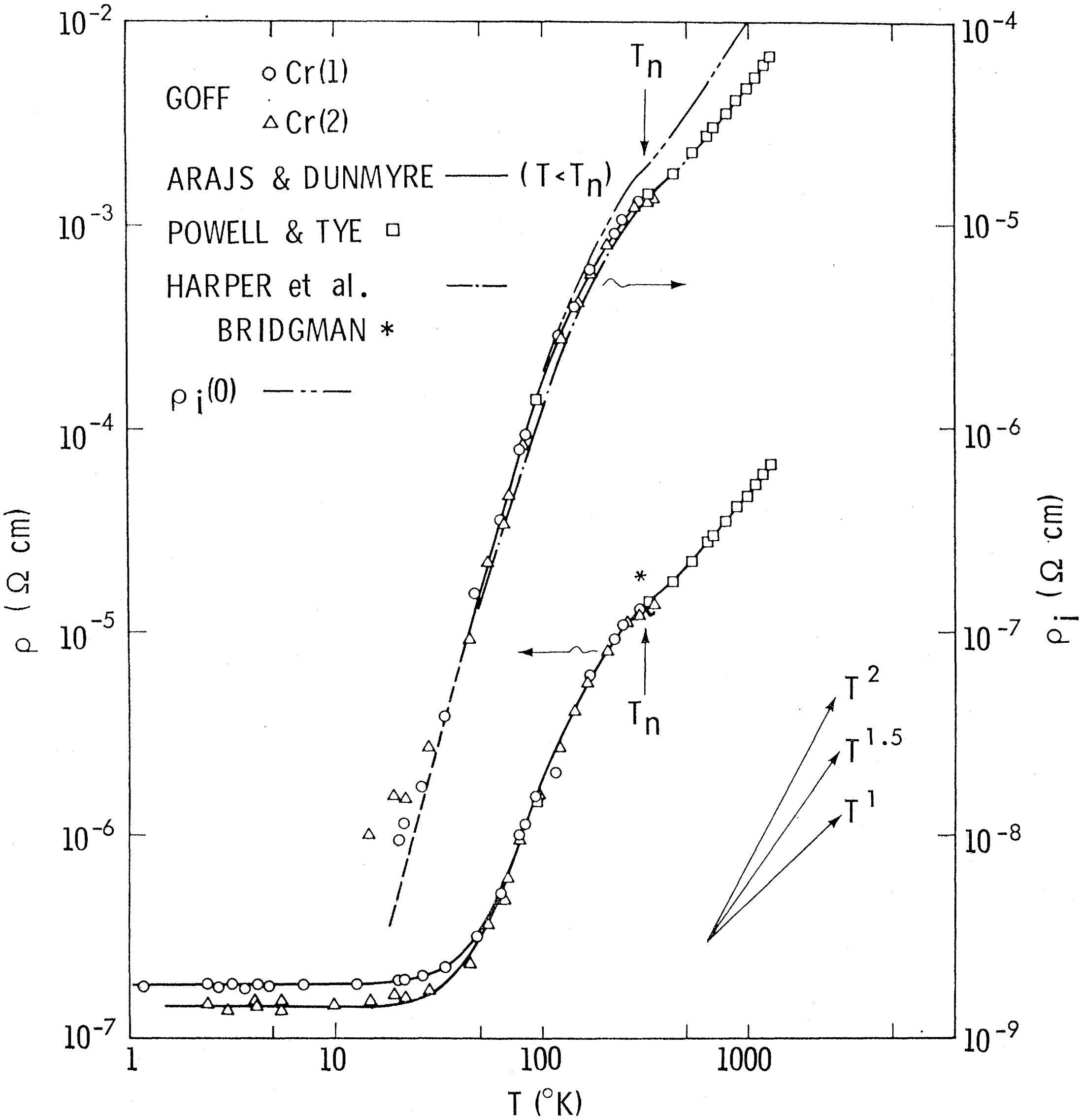

FIG. 2. Electrical resistivity of the present measurements shown compared with some other measurements extant. Both the total resistivity ρ and the ideal resistivity ρ_i are shown. The top-most curve $\rho_i(0)$ is the scattering factor derived from ρ_i by means of the model.

Tye indicates an increase in the neighborhood of T_n. de Morton,[13] and Marcinkowski and Lipsitt[11] showed that plastic deformation lowers ρ at temperatures below T_n and raises it at higher temperatures. Clearly, Matthiessen's rule is not obeyed at temperatures on the order of T_n and above.

It may well be that some of these peculiarities result from the effect of preparation on the magnetic structure of the material. Sabine and Cox[14] showed that plastic deformation changes the magnetic structure of the material without affecting T_n, and it is known that field cooling of Cr through T_n changes its magnetic symmetry.[15,16] Recently, Goff[17] concluded from a comparison of the transport properties of Cr-like and Cr alloys that the transport properties of the Cr alloys depends upon their magnetic symmetry.

The temperature dependence of ρ_i is anomalous over the whole temperature range. The most striking anomaly, the well-known cusp minimum seen at T_n,[5,18] is small. The difference in the extrapolated data above and below the cusp[5] is only about 2%. From the point

---

[13] M. E. de Morton, Nature **181**, 478 (1958).

[14] T. M. Sabine and G. W. Cox, J. Phys. Chem. Solids **27**, 1955 (1966).

[15] R. A. Montalvo and J. A. Marcus, Phys. Letters **8**, 151 (1964).

[16] A. J. Arko, J. A. Marcus, and W. A. Reed, Phys. Rev. **176**, 671 (1968).

[17] J. F. Goff, J. Appl. Phys. **39**, 2208 (1968).

[18] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **68**, 27 (1933).

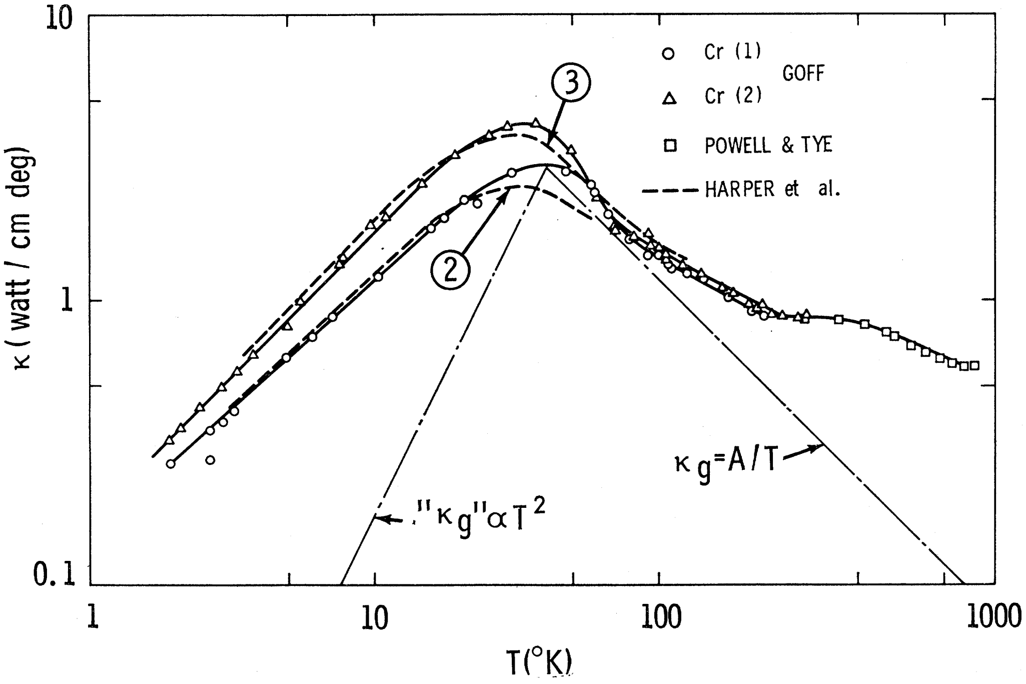

FIG. 3. Total thermal conductivity of the present measurements shown compared with some other measurements extant. The lower double dashed line is the upper bound for the lattice component κ_g which has been estimated from theory.

of view of this paper the anomalous behavior away from T_n is the more interesting.

Below 100°K, ρ_i varies as $T^{3.2}$.[19] This dependence has been ascribed[6] to a mixture of *s-d* and *s-s* scattering. Between 150 and 250°K it shows an approximate $T^{1.8}$ dependence[17] that has not been explained. However, since this exact magnitude and temperature dependence are seen in the nominally nonmagnetic TiFe[17] it implies a large amount of electron-electron scattering. Above T_n there is a concavity.[1,11,20,21] This anomaly is generally assumed to result from a precursor of the lower-temperature antiferromagnetic state.[21] However, it extends to about 800°K in Powell and Tye's data and is consistent with the model being proposed to explain the anomalous behavior of L in this temperature range.

B. Thermal Conductivity

The thermal-conductivity data of samples Cr(1) and Cr(2) have been compared in Fig. 3 with those of Powell and Tye's[1] most annealed sample and with Harper's[6] samples that have similar ρ_0's (the sample parameters are given in Table I). At T_n the agreement with Powell and Tye is within experimental accuracy. At lower temperatures it is seen that these data differ from those of Harper; but since the measurement is less accurate than that of ρ, no conclusions can be drawn.

The most general case in a magnetic material is that the thermal conduction is the sum of three conduction processes:

$$\kappa=\kappa_e+\kappa_g+\kappa_m\,, \tag{4.2}$$

electronic, lattice, and magnetic, respectively. One can not be certain of the magnitudes of the contributions of the individual components; but since κ_e usually predominates in elemental metals with $\rho_0 \leq 10^{-6}\ \Omega$ cm,[22] let it be assumed for the moment that $\kappa=\kappa_e$ alone and that only one electron group contributes substantially to it. Then, if this electron group is reasonably degenerate (metallic assumption), there exists a thermal analog of Matthiessen's rule[22]

$$\kappa_e^{-1}=w=w_0+w_i\,, \tag{4.3}$$

where the thermal resistivity w is the sum of the residual and ideal resistivities, respectively. w_0 is related to ρ_0,

$$w_0=\rho_0/L_0T\,, \tag{4.4}$$

and w_i is the result of the intrinsic electron-phonon interaction of the solid. At low temperatures it varies as T^2 and becomes constant at higher ones.[23] As a result w has a minimum (κ_e a maximum) at about $\frac{1}{10}$ of the Debye temperature Θ. The observed maxima shown in the figure fall between 35 and 45°K and so are compatible with $\Theta(\mathrm{Cr})=405$°K.[24]

---

[19] S. Arajs, R. V. Colvin, and M. J. Marcinkowski, J. Less-Common Metals 4, 46 (1962).

[20] J. E. Cox and W. H. Lucke, J. Appl. Phys. **38**, 3851 (1967).

[21] D. B. McWhan and T. M. Rice, Phys. Rev. Letters **19**, 846 (1967).

[22] P. G. Klemens, Solid State Phys. **7**, 1 (1958).

[23] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1954).

[24] I. Esterman, S. A. Friedberg, and J. E. Goldman, Phys. Rev. **87** 582, (1952).

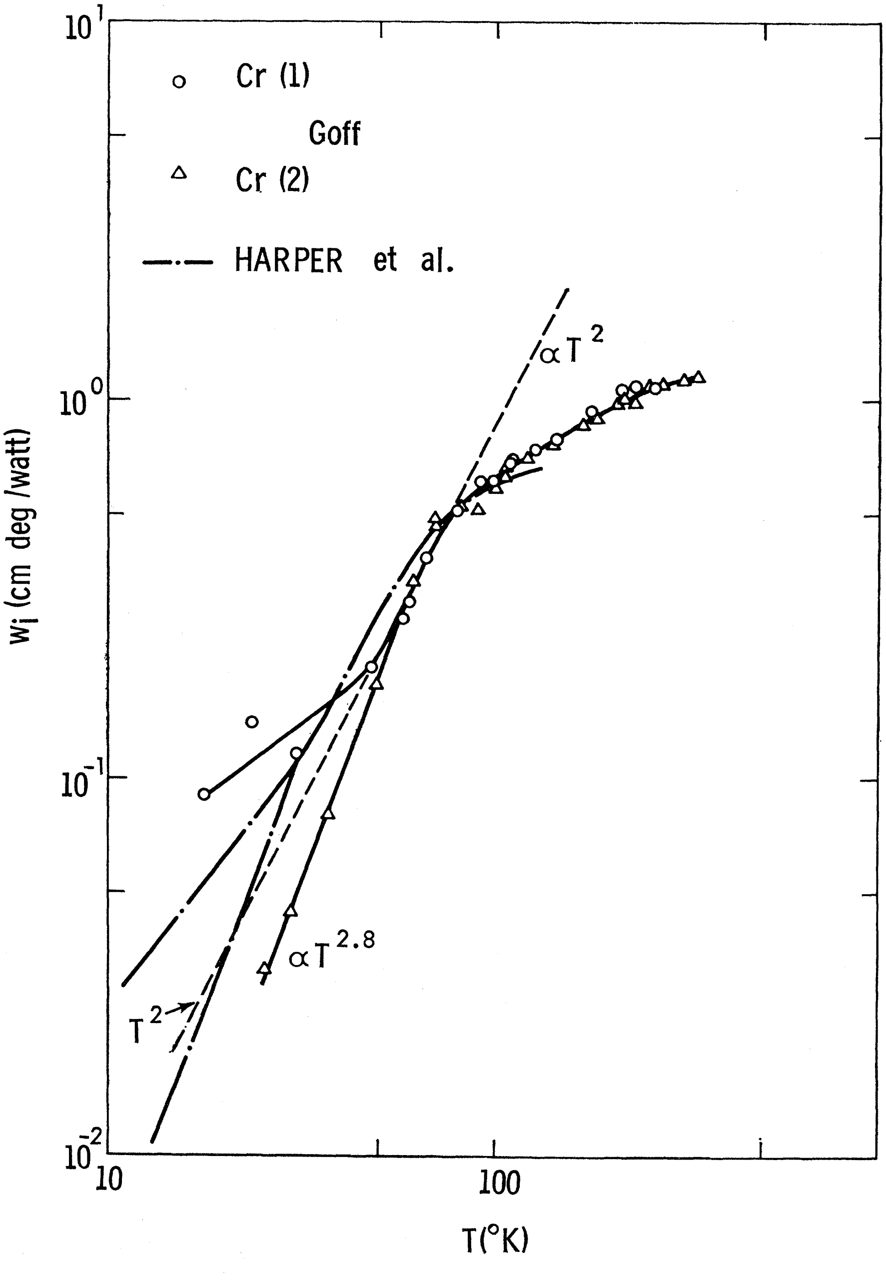

Fig. 4. Ideal component of the thermal resistivity derived from the present measurements. The double dashed line is from Harper *et al.* (Ref. 6), Fig. 3.

Below these maxima where w_0 predominates, κ is ordered with $1/\rho_0$ for all the data. However, above the maxima where w_i and ρ_i become important, these data again differ from those of Harper.

The values of w_i shown in Fig. 4 were obtained from the actual data by use of Eqs. (4.3) and (4.4) and the ρ_0's in the table. Above 55°K, w_i is unique—as would be expected of an intrinsic property of the solid—and has the expected T^2 behavior over a small range of temperature (about 20°K). At still lower temperatures, it shows the strange behavior first noted by Harper and co-workers (dashed line in Fig. 4) and which is still not understood. It may be that there is some magnetic effect.

On the basis of what has been said above, one would expect κ to become temperature-independent at high temperatures. However, just below T_n there seems to be a slight minimum; and the temperature-independent region above T_n is short. Thus, while the qualitative behavior of κ at the lower temperatures is clearly consistent with there being only an electronic component of the thermal conductivity, at higher temperatures κ is anomalous.

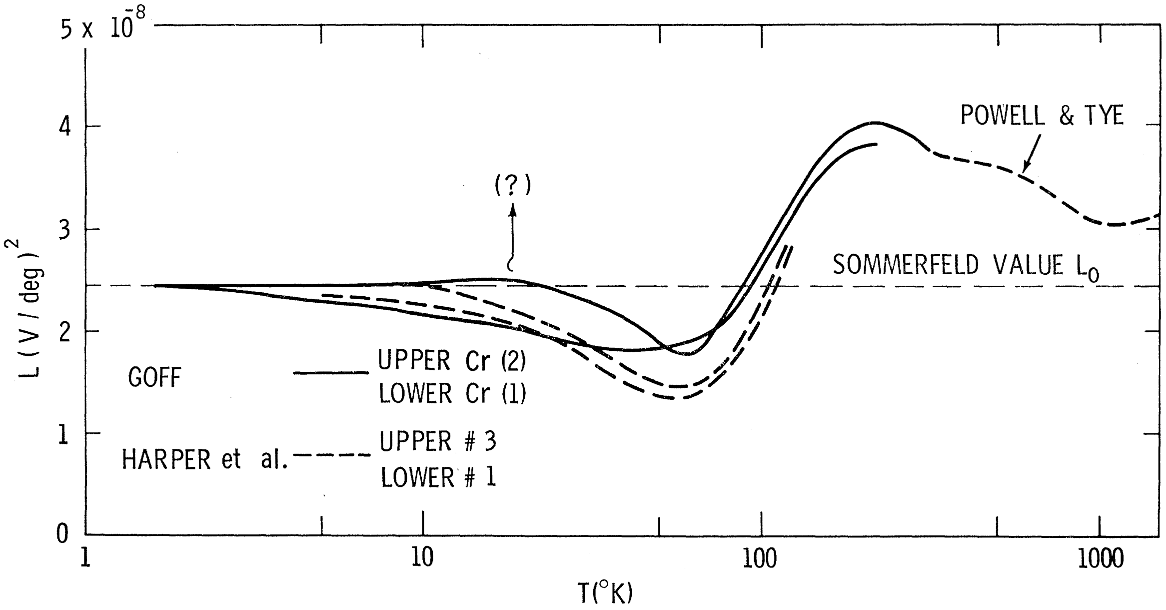

FIG. 5. Total Lorenz number of the present measurements shown compared with other measurements extant.

Finally, there appears to be no detectable anomaly at the spin-flip temperature (122°K).

C. Lorenz Number

The measured Lorenz number $L=\kappa\rho/T$ shown by the solid lines in Fig. 5 was calculated from the data for κ shown in Fig. 3, the ρ_0 given in Table I, and $\rho_i(T)$ of Arajs in order to minimize the relative error in ΔL at temperatures above 100°K. The agreement with Powell and Tye at T_n is within experimental error (about 10%). The lower temperature dashed lines were constructed from Harper's data in the same manner but with his $\rho_i(T)$ shown in Fig. 2.

In the metallic case, $L=L_0$ whenever the electron scattering processes are elastic: at low temperatures where $\rho=\rho_0$, and at higher ones where $T\geq\frac{1}{2}\Theta$. At the intervening temperatures $L<L_0$. It can be seen that L(Cr) behaves qualitatively like a metal below 90°K, while at higher temperatures it is much greater than L_0 at all temperatures and shows an inflection at T_n. The data for Cr(2) indicate L to be slightly greater than L_0 at 15°K. Possibly $\kappa_m\neq 0$ at these temperatures.

The high temperature, anomalous ΔL is shown more clearly in Fig. 6. Its essential characteristics are that (a) it increases upon anneal, (b) between 120 and 170°K it varies as T^2 within experimental error, (c) at all higher temperatures up to 1000°K it decreases, (d) and the rate of decrease changes at T_n. This paper does not consider the data above 1000°K.

V. ANALYSIS

A. Lattice Thermal Conductivity

Although it has been shown in the previous sections that at the lower temperatures both κ and L behave as if the thermal conductivity consisted of only an electronic component (except perhaps near 15°K), the question remains as to whether a lattice component could be responsible for ΔL at the higher temperatures. The separation of κ into components is difficult,[22] and κ_g(Cr) has not been determined. The following discussion of κ_g treats only the theoretical values of simple metals. Since phonons in transition metals can be expected to undergo more complicated scattering processes,[25] these theoretical values serve only as an upper bound.

A maximum in κ_g—usually observed to occur at about $\frac{1}{10}\theta$ (Refs. 26 and 27)—would occur at approximately the same temperature as the measured maxima in Fig. 3. Below this maximum the electron-phonon interaction causes $\kappa_g\propto T^2$; above it, umklapp and point-defect interactions cause a T^{-1} variation. If only umklapp processes are important above the maximum, the Leibfried and Schloemann formula[22,28] predicts that ultimately $\kappa_g=A_u/T$. If Klemens' values[22] of this calculation are taken but with $\theta=405$°K,[24] it is found that $A_u=116$ W/cm. The resulting upper bound is shown in Fig 3 by the dashed line. The lower-temperature values proportional to T^2 have been placed so that κ_g(max) occurs at $\frac{1}{10}\theta$. Thus it is seen that between about 50 and 100°K the theoretical calculation would imply that κ is predominately κ_g. Not only does this conclusion contradict the qualitative behavior discussed in the preceding sections but also in simple metals κ_g(100°K) is only about 10% of the total.[26,27]

---

[25] R. Fletcher and D. Greig, Phil. Mag. **16**, 303 (1967).

[26] G. K. White and S. B. Woods, Can. J. Phys. **33**, 58 (1955).

[27] W. R. G. Kemp, P. G. Klemens, R. J. Tainsh, and G. K. White, Acta Met. **5**, 303 (1957).

[28] G. Leibfried and E. Schloemann, Nachr. Akad. Wiss. Göttingen, Math. Physik Kl. IIa **4**, 71 (1954).

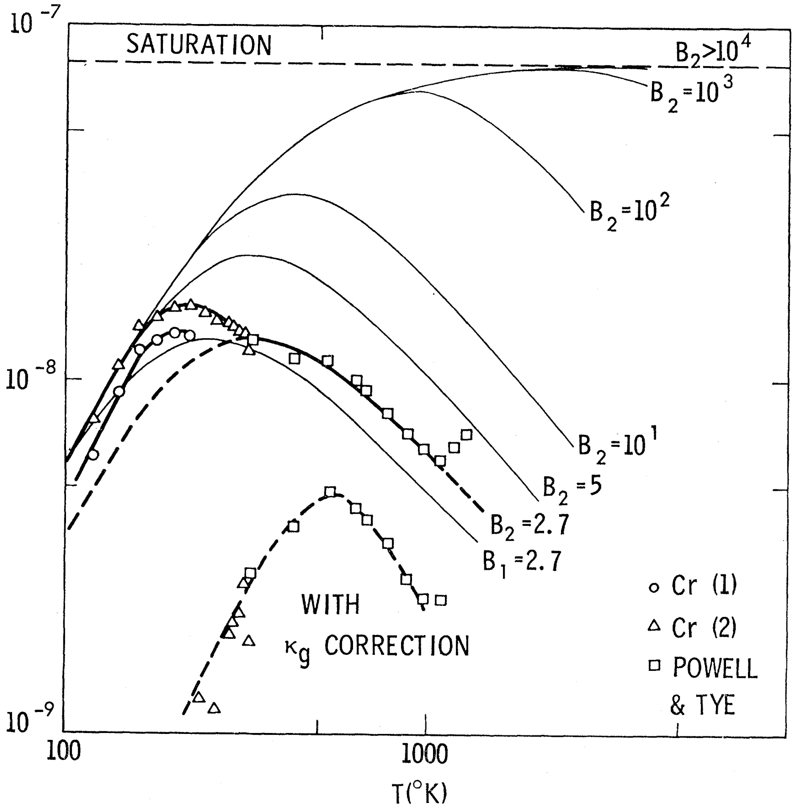

FIG. 6. Excess Lorenz number $\Delta L=L-L_0$ (where L_0 is the Sommerfeld value) shown compared with calculations from the model. (B_1, $C_1=330$ eV^{-2}) are the constants applicable to Cr(2) below T_n; (B_2, $C_2=195$ eV^{-2}) are the constants applicable to Powell and Tye's data above T_n. The lowest curve, which is ΔL corrected by an estimated value of the lattice thermal conductivity, is shown to emphasize that this anomaly is not likely due to lattice conduction.

This calculation of κ_g is almost certainly too large. The Leibfried-Scholemann formula itself gives values that are about three times those that are observed.[22] Further, point-defect interactions which also give $\kappa_g=A_p/T$ would further reduce κ_g.

Moore and co-workers[4] assumed that

$$\kappa=LT/\rho+A/T \qquad (5.1)$$

and deduced that $L=2.80\times10^{-8}$ V^2/deg^2 and $A=A_uA_p/(A_u+A_p)=80$ W/cm. Not only is L still anomalously large but also the constant A is still rather large in consideration of the arguments given above. If ΔL is recomputed by first reducing κ by A/T, then, as can be seen in Fig. 6, the anomaly is not eliminated but only shifted to higher temperatures.

Therefore, to explain the anomaly in ΔL in terms of a lattice component, this κ_g must be anomalously large at the higher temperatures and must behave anomalously at the lower ones. Such unique behavior of the phonon-conduction processes responsible for κ_g would be surprising because they tend to occur in the long-wavelength modes[10,29] which are only slightly dependent on the particular substance.

Thus, while it is realized that there is probably some lattice component that affects ΔL, in the following it is assumed that it is negligible. It is seen that the resulting analysis in terms of an anomalous κ_e has a physical basis which is more compatible with the known band structure of Cr and its behavior near T_n.

B. Method of Moments

The method of moments (hereafter MM) as formulated by Klemens[7] is a way of treating the Boltzmann equation so that the resulting transport coefficients become integral functions of energy only. In this form they can be readily adapted to substances with complicated band structures where the distributions of states and scattering processes about the Fermi level are likely to be complicated. It differs from other formulations[30,31] by choosing the Fermi level as its reference energy. In this way the difficult problem of the temperature dependence of the Fermi energy in a substance with a complicated band structure is avoided; it is changed to the problem—which proves easier—of the temperature dependence of the distribution of states and scattering processes about the Fermi level.

The transport coefficients generally consist of double integrations over a constant energy surface and energy. The MM replaces the integration over the constant energy surface by a purely formal function $\sigma(\epsilon)$, which is called here the specific conductivity. ϵ is the reduced energy E/KT. This function can be expanded about the

---

[29] J. F. Goff and N. Pearlman, Phys. Rev. **140**, A2151 (1965).

[30] H. Jones, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 19 p. 227.

[31] F. J. Blatt, J. Phys. Chem. Solids **17**, 177 (1961).

Fermi level so that the first terms of the expansion can be determined by the data.

If it is assumed that a relaxation time exists which is the same for the electrical and thermal processes and that the phonon system is in equilibrium, then the transport coefficients become
electrical conductivity

$$\sigma = M_0, \tag{5.2a}$$

thermal conductivity

$$\kappa_e = (K/e)^2 T (M_2 - M_1^2/M_0), \tag{5.2b}$$

Lorenz No.

$$L = (K/e)^2 (M_2/M_0) - S^2, \tag{5.2c}$$

thermoelectric power

$$S = (K/e)(M_1/M_0). \tag{5.2d}$$

M_n is the nth moment of $\sigma(\epsilon)$,

$$M_n = -\int_{-\infty}^{+\infty} \epsilon^n \sigma(\epsilon) \frac{\partial f_0}{\partial \epsilon} d\epsilon,$$

where f_0 is the Fermi-Dirac distribution function. It is possible to neglect the S^2 term in Eq. (5.2c) [and similarly the M_1^2/M_0 term in Eq. (5.2b)] because $M_2/M_0 > 1$, $(K/e) = 86.3$ μV/deg, and $S_{\max}(\mathrm{Cr}) = 20$ μV/deg at 300°K.[32] This neglect causes only about a 6% error, and so in the following formulas these terms are no longer included. However, because of the magnitude of S there may well be some structure in κ_e and L near T_n that is beyond the precision of these data.

Let the expansion of $\sigma(\epsilon)$ about the Fermi level be

$$\sigma(\epsilon) = \sigma_0 + \sigma_1\epsilon + \tfrac{1}{2}\sigma_2\epsilon^2 + \tfrac{1}{6}\sigma_3\epsilon^2 + \cdots, \tag{5.3}$$

where $\sigma_m = (\partial^m\sigma/\partial\epsilon^m)_0$. If only the first term in this expansion which makes M_n nonvanishing is retained, the coefficients in Eqs. (5.2) have the normal metallic form. If the second nonvanishing term is retained, they become

$$\sigma = \sigma_0 + \tfrac{1}{6}\pi^2\sigma_2, \tag{5.4a}$$

$$\kappa_e \approx (K/e)^2 T[\tfrac{1}{3}\pi^2\sigma_0 + (7\pi^4/30)\sigma_2], \tag{5.4b}$$

$$L \approx \tfrac{1}{3}\pi^2 \left(\frac{K}{e}\right)^2 \frac{[1 + (7\pi^2/10)(\sigma_2/\sigma_0)]}{[1 + \frac{1}{6}\pi^2(\sigma_2/\sigma_0)]}, \tag{5.4c}$$

$$S = \left(\frac{K}{e}\right) \frac{[\frac{1}{3}\pi^2\sigma_1 + (7\pi^4/10)\sigma_3]}{[\sigma_0 + \frac{1}{6}\pi^2\sigma_2]}. \tag{5.4d}$$

Since these formulas are expressed in terms of the reduced energy, the σ_m depend implicitly on temperature. In addition to the temperature dependence of the inherent scattering processes, it is easy to see by comparing the expansions of $\sigma(E)$ and $\sigma(\epsilon)$ that

$$(KT)^m \sigma_{mE} = \sigma_m. \tag{5.5}$$

Thus, the explicit temperature effects of the higher terms in Eq. (5.3) become apparent.

Properly speaking, L is not a transport coefficient. However, it has the advantage that it becomes equal to L_0 for a normal metal whenever the assumptions made at the beginning of this section hold. Therefore the second-order effects are more easily seen in $\Delta L = L - L_0$:

$$\frac{\Delta L}{L_0} = \left(\frac{16}{15}\right)\left(\frac{\sigma_{2E}}{2\sigma_{0E}}\right)(\pi KT)^2 \Big/ \left(1 + \tfrac{1}{3}(\pi KT)^2 \frac{\sigma_{2E}}{2\sigma_{0E}}\right). \tag{5.6}$$

ΔL has a saturation value of 7.815×10^{-8} V^2/deg^2 or about 3.2 times L_0.

The assumptions made in MM, that were given above, might be expected to hold at temperatures near 100°K; for ρ_i changes from its low-temperature slope to its high temperature one at that temperature. Certainly it can be seen in Fig. 6 that the temperature dependence of ΔL between about 120 and 170°K is apparently the same as the initial temperature dependence of Eq. (5.6),

$$\Delta L/L_0 \approx (16/15)(\pi K)^2 (\sigma_{2E}/2\sigma_{0E}) T^2. \tag{5.7}$$

The quantity $C = (\sigma_{2E}/2\sigma_{0E})$ has been determined from the data shown in the figure to be Cr(1), $C = 270$ (eV)$^{-2}$; Cr(2), $C = 330$ (eV)$^{-2}$.

The increase in ΔL upon anneal is consistent with the multiband point of view (see the Appendix) developed by Gallo[33–35] to account for similar effects in rare earths and semimetals. In these terms ΔL is caused by the partial thermoelectric powers of overlapping bands. In turn, the thermoelectric power will increase as the matrix becomes more orderly upon anneal.[36]

C. Model

It was shown in Sec. V B that from the electronic point of view the values of $\Delta L > 0$ seen below T_n in Fig. 6 are caused by terms of at least second order in the expansion of $\sigma(E)$. Therefore, $\Delta L > 0$ above T_n implies that these terms persist. Either C becomes temperature-dependent above 170°K and slowly decreases or the range of E over which the higher-order terms extend is limited, and as the temperature is raised give a smaller and smaller contribution to the integrals. Later, it is seen that the second point of view is more physically real.

---

[32] A. L. Trego and A. R. Mackintosh, Phys. Rev. 166, 495 1968).

[33] C. F. Gallo, R. C. Miller, P. H. Sutter, and R. W. Ure, Jr., J. Appl. Phys. 33, 3144 (1962).

[34] C. F. Gallo, B. S. Chandrasekhar, and P. H. Sutter, J. Appl. Phys. 34, 144 (1963).

[35] C. F. Gallo, J. Appl. Phys. 36, 3410 (1965).

[36] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).

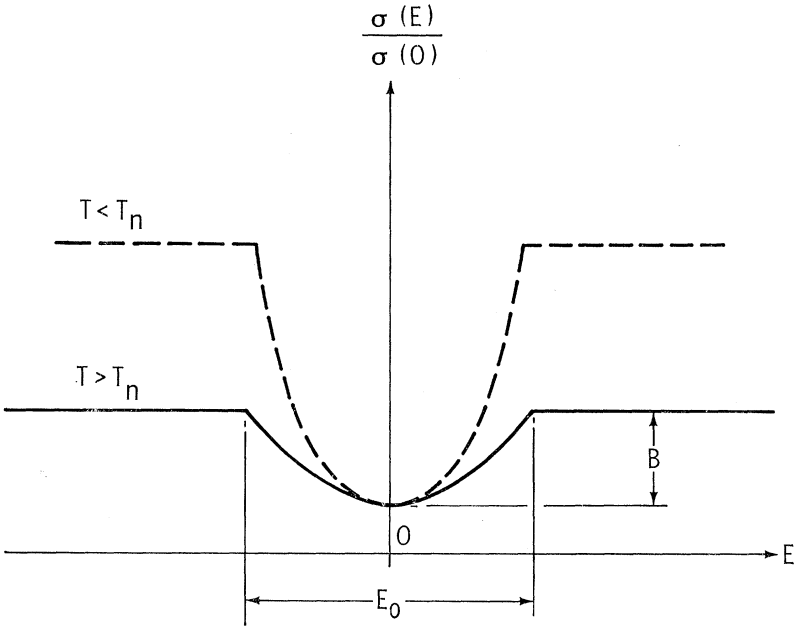

FIG. 7. Schematic of the model for the reduced specific conductivity $\sigma(E)/\sigma(0)$.

The model chosen is shown in Fig. 7 by the solid line; the dashed line represents the model applicable at the lower temperatures. For even values the nth moment integrals of Eqs. (5.2) can be expressed in terms of definite Fermi-Dirac integrals $F_n(\epsilon_0)$:

$$M_n(\epsilon_0)=\{\sigma_{10}F_n(\epsilon_0)+\sigma_{20}[F_n(\infty)-F_n(\epsilon_0)] +\tfrac{1}{2}\sigma_2F_{n+2}(\epsilon_0)\}, \quad (5.8)$$

where

$$F_n(\epsilon_0)=-\int_{-\epsilon_0/2}^{+\epsilon_0/2}\epsilon^n\frac{\partial f_0}{\partial\epsilon}d\epsilon,$$

and σ_{20}/σ_{10} represents $\sigma(\frac{1}{2}E_0)/\sigma(0)$. Since L is proportional to M_2/M_0, it is convenient to define a new function

$$G_n\equiv M_n/\sigma_{10}. \quad (5.9)$$

Then the transport coefficients become

$$\sigma=\sigma_{10}(T)G_0(\epsilon_0,T), \quad (5.10a)$$

$$\kappa_e\approx\sigma_{10}(T)(K/e)TG_2(\epsilon_0,T), \quad (5.10b)$$

$$L\approx\left(\frac{K}{e}\right)^2\frac{G_2(\epsilon_{0,T})}{G_0(\epsilon_{0,T})}. \quad (5.10c)$$

Equation (5.10c) contains two constants that must be determined from the data: $B=\sigma_{20}/\sigma_{10}$ and E_0. These constants are related to the previously defined $C=4(B-1)/E_0^2$. In Fig. 6, Powell and Tye's data are shown fit by the solid line with $B=2.7$ and $C=195$ eV^{-2} ($E_0=0.187$ eV). The dashed line gives the extrapolation to lower temperatures. The family of light lines through the low-temperature data for Cr(2) have $B\geq 10$, $C=330$ eV^{-2}.

At 300°K $\epsilon_0=E_0/KT$ is 7.2. L is sensitive to such a large gap because the F_n (ϵ_0) in Eq. (5.8) do not approach their three-figure saturation values $F_n(\infty)$ until ϵ_0 attains rather large values: $n=0$, $\epsilon_0=16$; $n=2$, $\epsilon_0=19$; $n=4$, $\epsilon_0=28$. As a result, the values of E_0 that affect Eqs. (5.10) are comparable to the structure in the density of states of transition metals.[37,38]

The meaning of this model is apparent if $\sigma(E)$ is written in terms of its factors:[23]

$$\sigma(E)\propto N(E)v^2(E)\tau(E,T),$$

where N is the density of states, v is the group velocity of the carriers, and τ is their relaxation time. If there is only one interaction, then τ has the general form: $\tau=\phi(E)T^p$, where p is some power, and $\sigma(E)/\sigma(0)$ is independent of temperature. It is unlikely that τ would be more complicated over all energies and the whole temperature range. Therefore, $\sigma(E)/\sigma(0)$ is sensitive to scattering because of $\phi(E)$ but primarily represents band-structure properties. Its temperature dependence may well represent changes in the band structure. The dashed line representing the model at the lower temperatures becomes temperature-dependent at approximately $T/T_n=0.5$; B (which must be greater than 10) and C decrease until the high-temperature solid line is attained at T_n. The over-all model is symmetrical with respect to the Fermi level where it has a minimum.

It is possible to determine the temperature dependence of the scattering process and the variation of the band-structure properties at the Fermi level itself from Eq. (5.10a) and the measured values of $\rho_i(T)$ given in Fig. 2. The $G_0(T)$ determined from ΔL and the low-

---

[37] M. Asdente and J. Friedel, Phys. Rev. **124**, 384 (1961).
[38] L. F. Mattheiss, Phys. Rev. **139**, A1893 (1965).

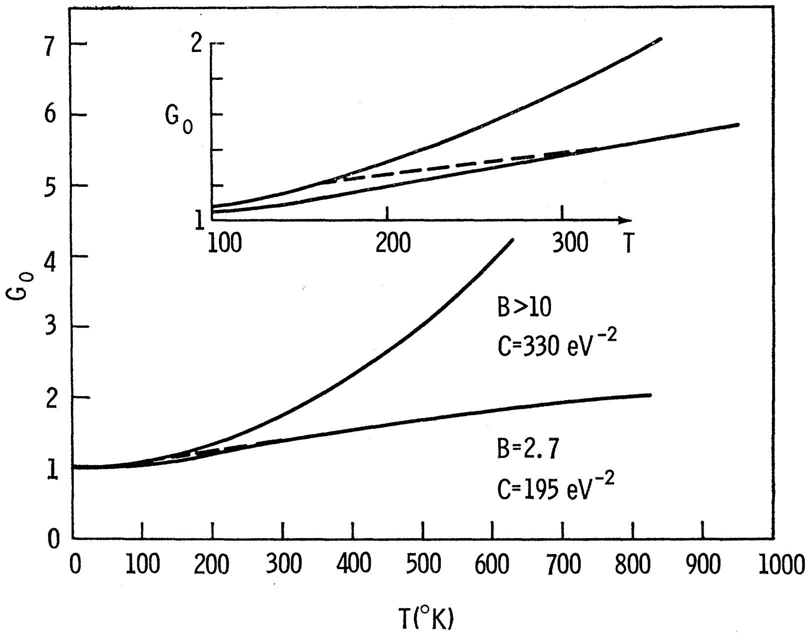

FIG. 8. Factor $G_0(T)$ derived by fitting $\Delta L(T)$ with the model. The dashed line between the lower-temperature model at 170°K and the higher temperature one at 310°K is an interpolation and is not expected to show the actual temperature dependence of the transition.

and high-temperature models are shown in Fig. 8. Since a straight line has been drawn between the 170 and 320°K values, any structure at T_n has been lost.

$\rho_i(0)=1/\sigma_i(0)$, which represents the intrinsic part of the scattering process, is shown in Fig. 2. The concavity noted previously has largely disappeared, and the inflection at T_n indicates that $\sigma(0)\propto N(0)v^2(0)\phi(0)$ has increased above T_n. Below T_n, $\rho_i(0)$ varies as T^2 over a brief range of temperature; above T_n the dependence is $T^{3/2}$.

VI. CONCLUSIONS

The theoretical calculation[39] of the Fermi surface of the paramagnetic phase of Cr existing above T_n indicates that it consists of four separate, simply connected pieces in a fcc Brillouin zone. The major portions are the two octohedra, one electronlike and the other holelike, that are responsible for the antiferromagnetic behavior below T_n.[39] The other two pieces are an electron and a hole lens of smaller size. The Fermi level intersects the bands that form the octohedra near their intersection point[37,39] so that they seem symmetrical about it. Shimizu and co-workers[40] have pointed out that the electronic heat capacity of Cr, which is anomalous at temperatures even above T_n, implies that the Fermi level occurs at a minimum in the density of states. Further, the coefficient of this heat capacity has a shoulder near 500°K.

Because the two octohedra are nearly congruent over a large portion of their surfaces, there is a spin-wave interaction that causes Cr to be antiferromagnetic below T_n.[39] At the Fermi surface, a temperature-dependent gap forms in a manner analogous to the BCS superconducting one. However, unlike the superconducting case, this gap moves off the Fermi surface in certain directions,[41] leaving conducting states in the gap. Consequently, below T_n the surface can be denoted as having a paramagnetic part (P) and an antiferromagnetic part (A).[21] These P portions of the surface can serve as reservoirs to supply carriers to the A portion.[42]

It is readily apparent that the model developed to explain $\Delta L(T)$ is very similar to this description of the Fermi surface and its behavior. The reduced specific conductivity $\sigma(E)/\sigma(0)$ shown in Fig. 7, which is expected mainly to represent band-structure quantities, has a minimum at the Fermi level and is symmetrical about it. The shoulder at $\pm\frac{1}{2}E_0$ could correspond to that seen in the heat capacity, for it would be seen at lower temperatures in the transport coefficients since they depend on higher order $F_n(E_0)$. Then, as one goes down in temperature, the opening of the gap at T_n would correspond to an increase in importance of the second-order terms of $\sigma(E)/\sigma(0)$—that is, in C, an increase in B, and a decrease in $\sigma(0)$ as states are removed from the Fermi level. Further, a superconducting gap[43] becomes nearly independent of temperature at $T/T_n\approx 0.5$, the temperature where the model becomes temperature-independent. Finally, to complete the analogy, the behavior of ΔL just below T_n is similar to that predicted by Cullen and Ferrell[44] for the acoustic

---

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

[40] M. Shimizu, T. Takahashi, and A. Katsuki, J. Phys. Soc. Japan **17**, 1740 (1962).

[41] T. M. Rice, A. S. Barker, Jr., B. I. Halperin, and D. B. McWhan, J. Appl. Phys. **40**, 1337 (1969).

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

[43] J. Bardeen and J. R. Schrieffer, *Progress in Low-Temperature Physics, III* (North-Holland Publishing Co., Amsterdam, 1961).

[44] J. R. Cullen and R. A. Ferrell, Phys. Rev. **146**, 282 (1966).

attenuation of transverse modes in superconductors where the increase of the density of states about the Fermi level at the transition temperature outweighs the decrease in carriers themselves.

Therefore, it is seen that the temperature dependences of the transport coefficients arise not only from scattering effects but are also distorted by band-structure effects that become ever more complicated as the Fermi skin thickens.[7] A measurement of the Lorenz number determines the temperature dependence of these band-structure factors in the coefficients, and the true temperature dependence of the scattering processes can be determined. Thus, while in Cr the behavior of $\rho_i(T)$ above 120°K indicates uncertain combinations of scattering processes, $\rho_i(0)\approx 1/\sigma(0)$ implies definite single processes below and above T_n. Below T_n, $\rho_i(0)\propto T^2$ probably implies electron-electron scattering[45]; for this temperature dependence is seen in nonmagnetic analogues of Cr.[17] Above T_n, $\rho_i(0)\propto T^{3/2}$, the temperature dependence which usually results from the phonon scattering of nondegenerate carriers.[23] There may be other explanations of this temperature dependence. However, it is consistent with the failure of Matthiessen's rule at these temperatures that has been noted in Sec. IV A and with the large value of the thermoelectric power.[32]

ACKNOWLEDGMENTS

The author would like to thank Professor P. G. Klemens for bringing to his attention the discussion of MM and for other helpful discussions. He also appreciates the help of A. C. Verbalis in making some of these measurements and W. J. Buehler in fabricating the sample.

APPENDIX: MULTIBAND ANALYSIS

The multiband thermal conductivity consists not only of the sum of the contributions of the individual bands $\sum_i \kappa_i$ but also of extra terms which correspond to the bipolar diffusion (currentless) of holes and electrons[35,46]

$$\kappa_e=\sum_i \kappa_i+\left(\frac{T}{\sum_i \sigma_i}\right)\sum_i \sum_j \sigma_i\sigma_j S_i(S_i-S_j)\,. \qquad \text{(A1)}$$

S_i is the thermoelectric power of band i, the partial thermoelectric power of the matrix. The other terms have been defined. These bipolar terms are well known to be important in semiconductors at high temperatures, and it has been recently pointed out by Gallo[33–35] that they become important in semimetals and rare earths. It is the purpose of this Appendix to show that the anomalous ΔL is consistant with this point of view.

The two-band formulation[46] of Eq. (A1) is

$$\kappa_e=\kappa_1+\kappa_2+\left(\frac{\sigma_1\sigma_2}{\sigma_1+\sigma_2}\right)T(S_1-S_2)^2\,. \qquad \text{(A2)}$$

If it is assumed that each band has a Lorenz No. L_0, then

$$L=L_0+\frac{\sigma_1\sigma_2}{(\sigma_1+\sigma_2)^2}(S_1-S_2)^2\,, \qquad \text{(A3)}$$

$$L\equiv L_0+\Delta L\,.$$

The previous moments analysis indicates that the integrands of the transport integrals composing L are symmetrical with respect to the Fermi level. Therefore, it is reasonable to assume that the conduction is occurring in overlapping hole and electron bands such that $\sigma_h=\sigma_e$ and $S_h=-S_e$. Then

$$\Delta L=S_e^2\,. \qquad \text{(A4)}$$

The simplest assumption is that $S_e(T)\propto T$, so that $\Delta L\propto T^2$ as is observed. Further, in the temperature range just below T_n where the antiferromagnetic energy gaps decrease with increasing temperature, one would expect the accompanying carrier-concentration increase to cause S_e and ΔL to decrease.

---

[45] N. F. Mott, Advan. Phys. **13**, 325 (1964).

[46] J. R. Drabble and H. J. Goldsmid, *Thermal Conduction in Semiconductors* (Pergamon Press, Inc., New York, 1961).