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Effect of molybdenum and vanadium on the lattice thermal conductivity and Lorenz number of chromium*

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The thermal conductivity and electrical resistivity of three Cr alloys with 3.89- and 9.35-at.% Mo and 4.57-at.% V have been measured in the temperature range from 3 to 300 K. The lattice thermal conductivity derived from these measurements is found to have maximum between 40 and 60 K and a magnitude at these temperatures that is much less than theoretical estimates. Point defects cannot explain these low magnitudes. Since the magnitude of the lattice thermal conductivity tends to increase as the Néel temperature of the alloy series decreases, there may possibly be phonon-magnon scattering present. All alloys show anomalously large values of the Lorenz number at temperatures above 100 K of the sort that has been seen in pure Cr. The lattice thermal conductivity is too small to explain this anomaly, and it must be an electronic effect as has been proposed.

I. INTRODUCTION

Some years ago, Powell and Tye[1] found that the high-temperature Lorenz number of chromium $L(L = K/\sigma T$, where K is the total thermal conductivity, σ is the electrical conductivity, and T is the temperature) was considerably larger than the expected Sommerfeld value $L_0 = 2.443\times 10^{-8}\ \mathrm{V^2/K^2}$. The usual explanation[2] for large values of L is that K consists of a lattice component K_g in addition to the electronic component K_e that is used to define L_0. In the present case this type of argument was first adduced by Moore *et al.*[3] and later by White,[4] who showed that an estimate of K_g which was obtained from properly scaled Cu-type theory could account for the magnitude of the anomaly. Powell and Tye[1] had thought that such values of K_g would be rather large. Indeed, one result of these large values was that the usual maximum found in K_g lay at the rather high temperature of 100 K. This temperature was about $\frac{1}{6}$ of the Debye temperature Θ rather than the more usual[2] $\frac{1}{20}\Theta$ to $\frac{1}{10}\Theta$. Another deficiency of this explanation was that it did not attempt to explain the structure found in [3,5,6]L at the Néel temperature ($T_N = 312$ K). Finally, it should be noted that Cu is a fcc metal while Cr is both bcc and antiferromagnetic. We are not aware of any experimental determination of K_g for even a bcc metal, and we shall see that in the present case there may also be magnetic effects.

As an alternative Goff[5,6] argued that the anomalous values of L could be attributed to electronic effects caused by chromium's peculiar band structure. In his analysis he assumed that K_g was negligible, and consequently the experimentally derived values of various constants were uncertain. Thus it is important from both points of view to obtain experimental values of K_g for Cr; and hopefully, to resolve the controversy about the meaning of the anomalous values of L.

The lattice thermal conductivity of a pure metal is obtained by alloying it with impurities in order to reduce the value of K_e with respect to K_g so that they may be more readily separated.[7] Consequently, we have measured K and the electrical resistivity ρ for three alloys over a temperature range from about 3 to 300 °K: 3.89-at.% Mo, 9.35-at.% Mo, and 4.57-at.% V (hereafter designated as 3.89 Mo, 9.35 Mo, and 4.57 V, respectively). Pure Cr and the Cr-Mo alloys are antiferromagnetic below about 200 K,[8,9] while the Cr-V alloy is paramagnetic at all temperatures.[10,11] These two types of alloys were chosen to explore the possibility that K_g depend upon magnetic effects.

It is well known that changes in the magnetic character of Cr are accompanied by changes in its band structure.[8,9] Therefore the present case is expected to be much more complicated than that of the noble metals where alloying does little other than change scattering processes. This complication has the effect of obscuring the meaning of the departures from Matthiessen's rule that are seen in ρ. We treat two kinds of these departures: Two-band departures that are expected in the paramagnetic Cr-V alloy and scattering departures that should be seen in both it and the Cr-Mo alloys. In addition, we consider that the departures seen in the antiferromagnetic Cr-Mo alloys are indicative of a progressive change of the conduction-band structure that occurs as T_N decreases rather than just scattering changes. It will be shown that although there is some uncertainty in the actual magnitude of K_g, its value and temperature dependence are determined well enough to resolve the problem of the meaning of L.

Sample preparation and experimental details are discussed in Sec. II. The total thermal conductivity and electrical resistivity are presented in

Sec. III. K_e is calculated in Sec. IV and used to separate K_g from K; K_g is discussed in Sec. V. The Lorenz number of Cr and the three alloys is discussed in Sec. VI. Section VII is the conclusion.

II. EXPERIMENTAL

The starting materials for the 3.89-Mo specimen were 99.996%-pure Iochrome obtained from Materials Research Corp. (Orangeburg, N. Y.) and 99.985%-pure molybdenum obtained from Jarrell-Ash (Waltham, Mass). The basic constituents were arc-melted together into a 50-g button and remelted two to three times to ensure homogeneity. Then the button was melted into the form of a crude bar. This was sealed in a quartz tube under vacuum and annealed for $1\frac{1}{2}$ h at about 825 °C. It was sawed into the shape of a bar approximately $4\times4\times60$ mm. The bar was sealed in a quartz tube under vacuum and annealed at 908 °C for 2 h. The tube was removed from the hot oven and allowed to cool in air. Nominal composition was 4.07 Mo, but wet chemical analysis indicated that the sample contained 3.89 Mo. The 4.57 V specimen was prepared in a similar way, the only exception being its annealing treatment. It was annealed for 2 h at 1025 °C followed by cooling at a rate of 41 °C/h to room temperature. The nominal V content was 3.89 at.% but chemical analysis yielded 4.57 at.%. Preparation of the 9.35-Mo specimen has been described previously.[12]

The thermal conductivity was determined by the steady-state method in an apparatus whose design has been described previously.[5] Heat was supplied at one end of the sample, and the temperature difference between two points along the length of the sample was determined by means of two thermometers. Above 77 K, two Rosemount model 118L platinum resistance thermometers were used. These were calibrated by the Navy Standards Laboratory to the specifications of the International Practical Temperature Scale of 1968 (IPTS-68).[13] The Callendar–Van Dusen equation[14] was used to interpolate between the calibration points of the first two thermometers. By this calibration procedure, temperatures could be measured to within 0.05 K of IPTS-68 by the first two thermometers, and to within 0.03 K of each other. Below 77 K, two $\frac{1}{10}$-W Allen Bradley carbon resistors (100-Ω room-temperature resistance) were used as thermometers. This technique has been described previously.[5] Temperature differences of 1–5 K were used above 10 K and differences of no less than 0.200 K below 10 K. All thermometer voltages and currents were measured with a Leeds and Northrup K-3 potentiometer.

The electrical resistance of the specimens was measured by the four-probe method with voltage contacts attached to the copper thermometer mounts. In the case of the 3.89-Mo and 4.57-V samples resistance was measured in the presence of a thermal gradient after the gradient had been measured. The effects of thermoelectric emf were eliminated by reversing the current. All resistance voltages were measured with a Leeds and Northrup K-3 potentiometer.

The random and systematic experimental error (excluding geometry) in resistivity was (1–2)% between 4 and 100 K and less than 1% elsewhere. The error in the geometric form-factor measurement was about 1%. Random and systematic errors in thermal conductivity such as radiation, thermal drift, and thermal emf's in the electrical circuits contributed about (2–3)%.

III. THERMAL CONDUCTIVITY AND ELECTRICAL RESISTIVITY

In Fig. 1, the total thermal conductivity K and electrical resistivity ρ of the two Cr-Mo alloys are plotted. The thermal conductivity rises rapidly with temperatures up to about 50 K and then increases more slowly. There is a relative minimum in the thermal conductivity of 9.35 Mo at about 230 K. The electrical resistivity ρ of both alloys is constant below about 30 K. The residual resistivity ρ_0 is listed in Table I. There is a relative minimum in the electrical resistivity at the Néel temperature T_N of each alloy; T_N is listed in Table I. The resistivity maximum below T_N is associated with opening of an energy gap over part of the Fermi surface.[12]

The total thermal conductivity and electrical resistivity of the 4.57 V specimen are plotted in Fig. 2. The thermal conductivity increases rapidly with temperatures below 80 K, but then levels off and begins to decrease at higher temperatures. Again, the electrical resistivity is constant below about 30 K (ρ_0 and Θ[15,16] are listed in Table I). This alloy is paramagnetic since T_N extrapolates to zero at about 3.7 V,[10,11] as is shown in Fig. 3. Consequently, there are no magnetic anomalies in ρ.

The ideal resistivity defined by

$$\rho_i = \rho - \rho_0$$

TABLE I. Sample data.

Sample	T_N (K)	ρ_0 ($\mu\Omega$cm)	Θ (K)	F_P (sec^3)
Pure Cr	312	0.0	587[a]	0.0
4.57 V	···	1.351	564[b]	2.08×10^{-46}
3.89 Mo	260	2.428	573[b]	2.92×10^{-43}
9.35 Mo	197	4.19	554[b]	6.06×10^{-43}

[a] Reference 15.

[b] Reference 16.

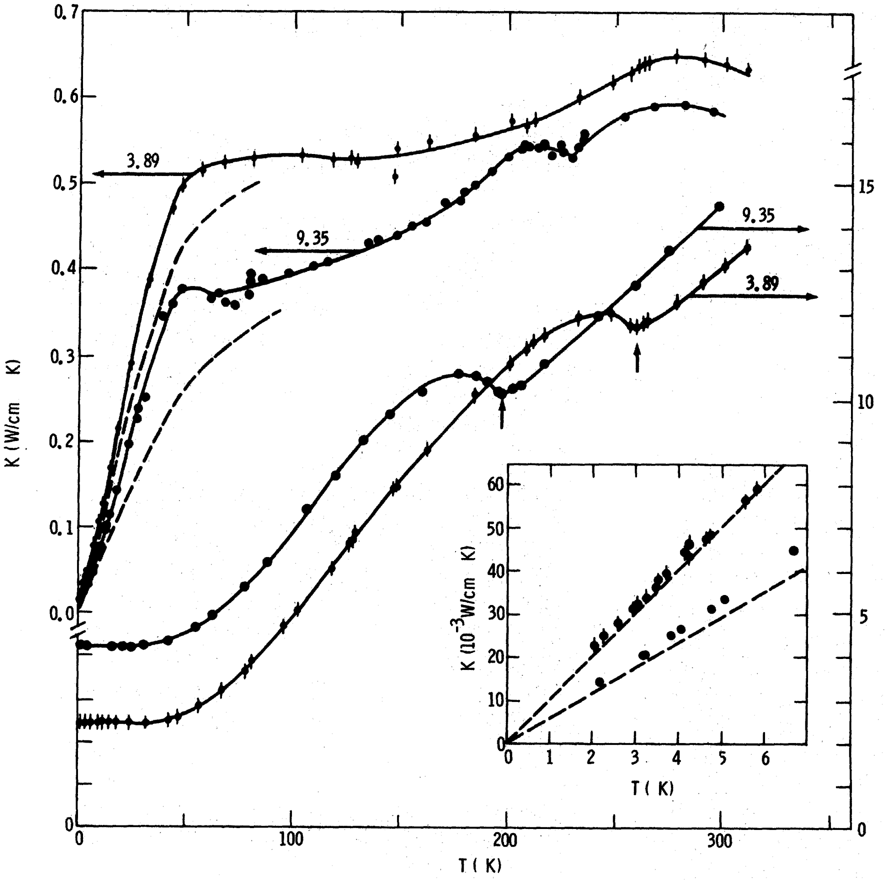

FIG. 1. Total thermal conductivity (upper two solid curves) and electrical resistivity (lower two solid curves) of two Cr-Mo alloys. The numbers are at.% Mo. The dashed lines are the calculated electronic thermal conductivity. The inset shows the thermal conductivity data at low temperatures.

is plotted in Fig. 4. Below 150 K, ρ_i of the two antiferromagnetic Cr-Mo alloys is higher than ρ_i^p (the p superscript meaning pure Cr) of pure Cr, but ρ_i of paramagnetic Cr-V is lower. There are obviously large deviations from Mathiessen's rule which will be taken into account shortly during the analysis of thermal conductivity. It is interesting that above T_N of pure Cr, at the limit of our ρ measurements, pure Cr has the highest ρ_i; ρ_i in the two Cr-Mo alloys (whose T_N's lower) is lower; and 4.57 V is still lower. This is suggestive of a resistance due to critical fluctuations.[17-19] However, one must first consider the effect on the electrical resistivity of band-structure changes due to alloying before any definite conclusions can be drawn. In any case, electron-phonon and impurity scattering are by far the largest resistive processes.

IV. CALCULATION OF K_g AND SEPARATION OF K_g

The lattice thermal conductivity K_g is obtained by subtracting the calculated values of the electrical thermal conductivity K_e from the total thermal conductivity K:

$$K_g = K - K_e . \qquad (1)$$

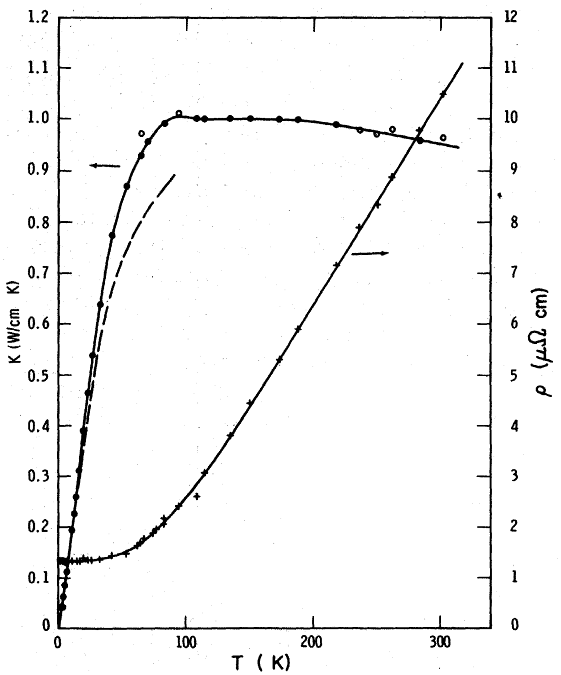

FIG. 2. Total thermal conductivity (upper solid curve) and electrical resistivity (lower solid curve) of Cr +4.57-at.% V. The dashed line is the calculated electronic thermal conductivity.

Thus the determined value of K_g depends upon the validity of the theory used to calculate K_e as well as the accuracy of the data for K.

The theory for calculating K_e utilizes the additive resistivity approximation[2] wherein

$$1/K_e = W = W_0 + W_i^p + \Delta W. \tag{2}$$

The total thermal resistivity W is nearly equal to the sum of the resistivities which arise from impurity- and phonon-scattering processes, respectively. The inexactness of this approximation, contained in the ΔW term, arises from the effect of alloying on W_i^p, the phonon thermal resistivity of pure Cr. There are a number of effects; and it is assumed here that ΔW can be taken to be their sum:

$$\Delta W = \Delta W^s + \Delta W^f + \Delta W^d + \Delta W^c, \tag{3}$$

which are departures from the additivity assumption for impurity and phonon scattering,[20] changes in the density of states of the Fermi surface, warping of the Fermi surface,[21] and two-band effects.[22] The inclusion of all these terms assures that K_g will be as large as conceivably possible.

Fortunately, impurity scattering dominates the resistivity processes in these alloys over a large temperature range; and its effect can be calculated exactly from the Wiedemann-Franz ratio[7]:

$$W_0 = \rho_0 / L_0 T, \tag{4}$$

where ρ_0 is the residual resistivity of the alloy. As a result, K_g can be determined rather accurately from the lowest temperatures up through its maximum. The purpose of this section it to show that the best estimates of the deviation terms ΔW do not change the magnitude and temperature of this maximum enough to vitiate our conclusions. The effect of ΔW is to prevent K_g from going to zero at temperatures just above the maximum.

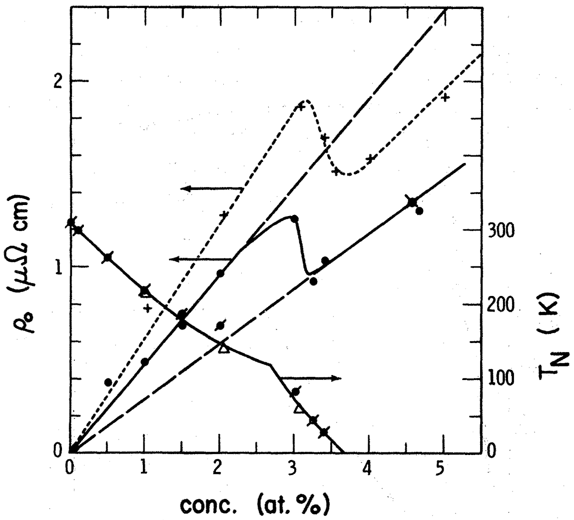

FIG. 3. Residual electrical resistivity and T_N of Cr as a function of concentration of V. The resistivity data are from Ref. 10 (●), Ref. 11 (+), and this work (●). The T_N data are from Ref. 10 (●) and Ref. 11 (Δ). There is a disagreement between the resistivity data of Ref. 10 and Ref. 11. We agree with the latter. However, both sets of data have a minimum in residual resistivity between 3 and 4 at.% which is associated with the elimination of antiferromagnetism.

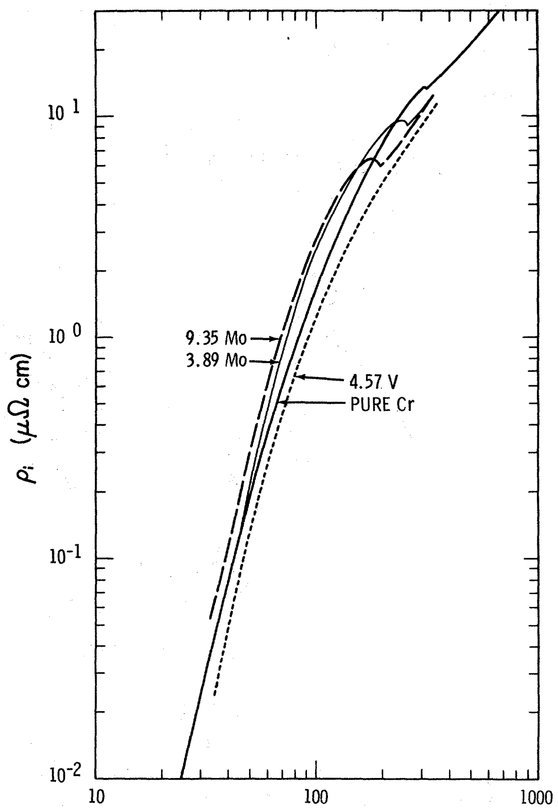

FIG. 4. Ideal electrical resistivity of the three Cr alloys of this work and pure Cr. The minima in ρ_i occur at T_N in Cr and the two Cr-Mo alloys.

There is a further complication in chromium that arises because its band structure and magnetic state are very intimately related. It has been shown that in the paramagnetic state conduction processes occur in two electron groups.[5,6,12,13,23] As the temperature is lowered, an antiferromagnetic transformation occurs that eliminates conduction in one of these electron groups at all lower temperatures. Thus Cr and these Cr-Mo alloys, which are in the antiferromagnetic state below about 200 K, can be considered single-electron group metals at these temperatures with similar W_i terms. However, Cr-V remains paramagnetic at all temperatures and consequently is a two-electron group conductor even at these low temperatures. The behavior of its ρ_i shown in Fig. 4 shows the expected reduction with respect to pure Cr as a result

TABLE II. Thermal-resistivity terms.[a]

Sample	T (K)	W_0	W_i^p	W_i^c	ΔW^s	ΔW^f	ΔW^d	ΔW^c	$\sum\Delta W$	$\sum\Delta W/W$
3.89 Mo	15	6.626	0.0367	...	+0.0092	−0.0022	+0.000	...	+0.007	0.001
	40	2.485	0.185	...	+0.050	−0.011	+0.000	...	+0.039	0.014
	55	1.800	0.318	...	+0.076	−0.019	+0.000	...	+0.057	0.026
	70	1.419	0.477	...	+0.099	−0.029	+0.160	...	+0.230	0.108
9.35 Mo	15	11.43	0.0367	...	+0.0092	−0.0062	+0.000	...	+0.003	0.000
	40	4.288	0.185	...	+0.050	−0.031	+0.020	...	+0.039	0.009
	55	3.119	0.318	...	+0.081	−0.054	+0.142	...	+0.169	0.047
	70	2.450	0.477	...	+0.113	−0.081	+0.260	...	+0.292	0.091
4.57 V	15	3.687	0.0367	0.024	+0.0017	...	+0.000	+0.0002	+0.0064	0.017
	40	1.383	0.185	0.123	+0.023	...	+0.0032	+0.0009	+0.036	0.023
	55	1.006	0.318	0.213	+0.050	...	+0.0035	+0.0015	+0.055	0.043
	70	0.790	0.477	0.316	+0.078	...	+0.0037	+0.0018	+0.068	0.058

[a] Thermal-resistivity units are cm K/W.

of the parallel conduction of this second electron group. One would expect a similar reduction in W_i, and so the two alloy systems must be treated separately.

It is expected then, that the simpler Cr-Mo alloys have a W_i that is similar to that of pure Cr. These data[5,24] are shown in Fig. 4 of Ref. 5. We have chosen to use the data of Harper *et al.*[24] below 70 K because we feel that they are more accurate in that temperature range. The peculiarities in W_i that are seen in both sets of data at the lower temperatures do not affect the analysis and have been ignored by extrapolation of the data to lower temperatures at T^2.

Ehrlich[20] recently treated ΔW^s, the deviation from the phonon thermal resistivity W_i that arises when impurity scattering is also present, by a variational method that assumes that the phonon scattering is completely inelastic. This assumption obtains at low temperatures but neglects elastic phonon scattering that begins as the temperature rises. The results of applying Ehrlich's calculation to these data are given in Table II. While there is some temperature dependence of the deviation, it results in about a 25% increase in W_i.

The deviation ΔW^f that arises because the Fermi surface of Cr may change with alloying can be estimated from existing data. Heiniger[16] determined the change of the coefficient of the electronic heat capacity at low temperatures. From these data it can be calculated that there is an increase in the density of states between Cr and Cr–9.35 Mo of a about 17%. Mitchell and Goff[12] actually determined the ratio R of the conduction processes of the antiferro- to the paramagnetic electron group for Cr and this same alloy. The change in $1/R$ is again about 17%. Although there may be some fortuity, it seems reasonable to assume that this change indicates growth of the low-temperature Fermi surface of about 6% for the 3.89-Mo alloy and 17% for the 9.35-Mo one. The effect of this growth is given in Table II.

Although the ideal electrical resistivity of pure Cr ρ_i^p would be expected to decrease with the addition of Mo because density of states of the conducting surface increases,[16] the data of Fig. 4 show an increase. The corresponding deviations from Matthiessen's rule shown in Fig. 5 are obtained from the equation

$$\rho = \rho_0 + \rho_i + \Delta\rho . \tag{5}$$

Although these deviations are quite small at the lower temperatures, at higher temperatures they approach values of 50% for 3.89 Mo and 65% for 9.32 Mo. Deviations of this magnitude are not unusual and are found even in noble metal alloys.[2] Klemens[21] has argued that deviations such as these could possibly arise from changes in large-angle-scattering processes. Since these processes are elastic, their effect on the thermal resistivity can be estimated by the Wiedemann-Franz ratio

$$\Delta W^d = \Delta\rho / L_0 T . \tag{6}$$

These deviations are given in Table II.

Since there are no other deviations for the single-electron-group Cr-Mo alloys, Eqs. (2) and (3) can be used to calculate K_e shown in Fig. 1 by the dashed line. Then the lattice thermal conductivity K_g given by Eq. (1) is plotted in Fig. 6. Although the theory is not so exact that the temperature dependence above the maximum can be determined with certainty, the deviations are too small to affect the magnitude and location of the maximum very much. These maxima lie near 45 K or about $\frac{1}{12}\Theta$, a reasonable temperature.

The calculation of K_e for the paramagnetic Cr-V specimen is more complicated because the existence of the second-electron group means that there are two-band effects. The ideal resistivities W_i^p and ρ_i^p will change to W_i^c and ρ_i^c, respectively; and

and two-band deviations ΔW^c and $\Delta\rho^c$ of the type discussed by Wilson[22] will appear in Eqs. (3) and (5), respectively.

If the two-electron groups are designated by 1 and 2, the conductivities of the ensemble are

$$\sigma=\sigma_1+\sigma_2\,, \qquad K=K_1+K_2\,. \tag{7}$$

If it is assumed as before that there are two sources of resistance in each electron group, then $1/\sigma_1=\rho_{01}+\rho_{i1}$; $1/\sigma_2=\rho_{02}+\rho_{i2}$; $1/K_1=W_{01}+W_{i1}$; $1/K_2=W_{02}+W_{i2}$. Then, no other deviations are considered, Mattiessen's rule becomes

$$\rho=\rho_0+\rho_i^c+\Delta\rho_i^c\,, \tag{8}$$

where

$$\rho_0=\frac{\rho_{01}\rho_{02}}{\rho_{01}+\rho_{02}}\,, \tag{9}$$

$$\rho_i^c=\frac{\rho_{i1}\rho_{i2}}{\rho_{i1}+\rho_{i2}}\,, \tag{10}$$

$$\Delta\rho=\frac{(\rho_{01}\rho_{i2}-\rho_{02}\rho_{i1})^2}{(\rho_{01}+\rho_{i1}+\rho_{02}+\rho_{i2})(\rho_{01}+\rho_{02})(\rho_{i1}+\rho_{i2})}\,. \tag{11}$$

Now define x_0 and x_i by

$$\rho_{01}=x_0\rho_{02} \tag{12}$$

and

$$\rho_{i1}=x_i\rho_{i2}\,. \tag{13}$$

With the substitution of these definitions, Eqs. (9)–(11) become

$$\rho_0=\frac{x_0}{x_0+1}\rho_{02}\,, \tag{14}$$

$$\rho_i^c=\frac{x_i}{x_i+1}\rho_{i2}\,, \tag{15}$$

$$\Delta\rho_i^c=\frac{\rho_{02}\rho_{i2}(x_0-x_i)^2}{[\rho_{02}(1+x_0)+\rho_{i2}(1+x_i)](1+x_0)(1+x_i^c)}\,. \tag{16}$$

The values of x_0 may be determined from the plot of ρ_0 versus concentration of vanadium in Fig. 3 in the following manner (the data used in Fig. 3 are from Ref. 11). Below 3 at.%, Cr-V is antiferromagnetic. Let band 1 be the magnetic band. Then because of the energy gap that opens when the alloy becomes antiferromagnetic, the carriers in band 1 freeze out; conduction at low temperatures occurs only in band 2. Therefore, Fig. 3 will give ρ_{02} below about 3-at.% V. Above 3-at.% V conduction occurs in both bands, and the curve in Fig. 3 gives ρ_0. Thus, from the ratio of the slopes above and below 3-at.% V,

$$\frac{\rho_0}{\rho_{02}}=\frac{x_0}{x_0+1}=0.621 \tag{17}$$

and $x_0=1.63$. Goff[5,6] has measured the ratio R of the conductivity in the magnetic band to the conductivity in the nonmagnetic band of pure Cr at high temperatures. $R=\sigma_{i1}/\sigma_{i2}=0.51$ or $x_i=1/R=1.96$. Now with $\rho_{i2}=\rho_i^p$ (the ideal resistivity of pure Cr in the nonmagnetic band), and with $\rho_{02}=2.18$ $\mu\Omega$ cm from Eq. (17) and Table I, it is possible to calculate ρ_i^c and $\Delta\rho_i^c$ from Eqs. (15) and (16), respectively. These calculations show, when compared with the measured ρ_i in Fig. 4, that there must be an additional deviation. We assume that this deviation is of the same type as appeared in the Cr-Mo alloys and write Eq. (8) as

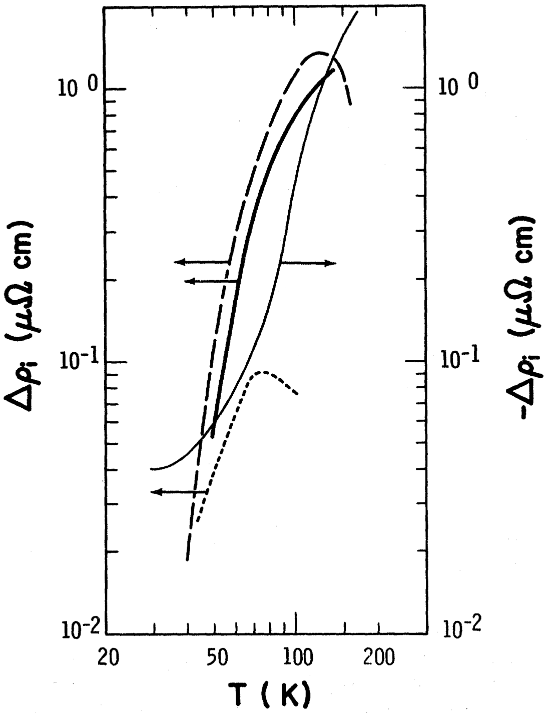

FIG. 5. Measured electrical-resistivity deviations from Mathiessen's rule ($\Delta\rho_i^c+\Delta\rho_i^d$). The dashed line is 9.35 Mo; the thick solid line is 3.89 Mo; and the thin solid line is 4.57 V (note that the deviations are negative for this sample). The thin dotted line shows deviations for 4.57 V when the ideal resistivity of pure Cr is corrected for two-band conduction.

$$\rho=\rho_0+\rho_i^c+\Delta\rho_i^c+\Delta\rho^d\,. \tag{18}$$

The difference $\rho-\rho_0-\rho_i^p$ between the measured ideal resistivity of 4.57 V and the measured ideal resistivity of pure Cr is negative and large in magnitude; it is the thin solid curve in Fig. 5. On the other hand the difference $\rho-\rho_0-\rho_i^c=\Delta\rho_i^c+\Delta\rho_i^d$ between the measured ideal resitivity of 4.57 V and the the calculated ideal resistivity of pure, paramagnetic Cr is both smaller in magnitude and positive; it is the dotted line in Fig. 5. In other words, the fact that the ideal resistivity of 4.57 V is less than the ideal resistivity of pure Cr is a manifestation of the two-band nature of this alloy, and $\Delta\rho_i^c$ must exist. However, calculations show that $\Delta\rho_i^c$ is at

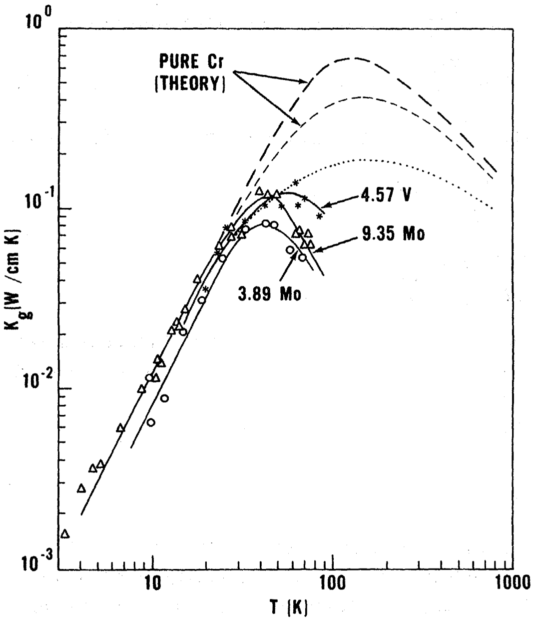

FIG. 6. Lattice thermal conductivity. The three solid curves are experimental and were constructed from the best curve drawn through the data. The points on these curves are the reduction to K_g of the actual data points of K. The two dashed curves were constructed from White's estimate (4) of the values of the phonon-electron and umklapp thermal resistivities needed to explain the anomalous high-temperature Lorenz number (see Fig. 7). The upper dashed curve is the additive resistivity approximation; the lower dashed curve is an integral calculation. The dotted curve shows the effect of adding 9.35-at.% Mo as point defects.

most 10% of $\Delta\rho_i^d$, and is generally less than that.

A set of equations that are analogous to Eqs. (14)–(16) can be derived for the thermal resistivity:

$$W_0 = \frac{x_0}{x_0 + 1} W_{02}, \tag{19}$$

$$W_i^c = \frac{x_i}{x_i + 1} W_{i2}, \tag{20}$$

$$\Delta W_i^c = \frac{W_{02} W_{i2} (X_0 - X_i)^2}{[W_{02}(1 + X_0) + W_{i2}(1 + X_i)](1 + X_0)(1 + X_i)}, \tag{21}$$

where $W_{02} = \rho_{02}/L_0 T$ and $W_{i2} = W_i^p$. The three quantities W_0, W_i^c, and ΔW_i^c have been calculated; representative values are given in Table II. The deviations from Matthiessen's rule have been calculated in the same manner as for the Cr-Mo samples with W_i^c used in place of W_i^p. The values of K_e obtained are given by the dashed line in Fig. 2, and K_g is shown in Fig. 6. The maximum value of K_g lies near 60 K and the general trend seems to be that the magnitude of K_g increases as T_N approaches zero.

V. DISCUSSION OF K_g

The lattice thermal conductivity of all three alloys in Fig. 6 has a maximum between 40 and 60 K. Although the determination of K_g becomes susceptible to errors at temperatures near the maximum, the magnitude and temperature of the maximum are well determined. Below the maximum, $K_g \propto T^2$ to within experimental error. In the temperature range 2–6 K there is evidence for a weaker temperature dependence in Cr-Mo, but a more careful experiment is necessary in this range to draw definite conclusions. The lattice conductivity in 4.57 V is too small to be meaningfully separated below 15 K. Above the peak, the precise temperature dependence of K_g cannot be reliably determined; but it is between T^{-1} and T^{-2}.

It can be seen that 9.35 Mo has a higher K_g than 3.89 Mo. This trend is the reverse of what is found in most alloys,[2] i.e., usually K_g decreases with increasing impurity concentration. However, there is a precedent in the fcc alloys, where the addition of Ag impurities to Pd causes K_g to rise.[25] Klemens[2] has suggested that in Pd holes in the d band scatter phonons; the addition of Ag impurities fills the holes and reduces scattering. This type of situation could also obtain for Cr-Mo alloys, but considering that Cr and Mo are both in the same column in the Periodic Table, it is not obvious how Mo electrons can fill d holes.

There is another possible explanation for the rise of K_g with Mo concentration. Both of these alloys are antiferromagnetic in this temperature range, and there is the possibility of phonon-magnon scattering. It is observed that T_N of the Cr-Mo alloys decreases with increasing Mo concentration.[12] A phonon-magnon interaction which was weakened by the addition of Mo could lead to a decrease in phonon-magnon scattering and result in the observed rise of K_g. The fact that K_g for the vanadium alloy ($T_N = 0 K$) has a still higher magnitude above the maximum is consistent with this suggestion but not conclusive because the point-defect scattering important in this temperature range is also smaller. Point-defect scattering will be estimated below. In any event, no theoretical work has been done on the interaction of phonons with the itinerant spin density wave[9] found in Cr; and more experiments are necessary to establish that the observed decrease of K_g with increasing Mo concentration is the effect of magnetic scattering.

White[4] has estimated that for phonon-electron scattering in pure Cr, $K_E \approx 1.0 \times 10^{-4} T^2$ W/cm K. Our experimental value for 9.35 Mo (which obtains below the maximum), $K_E \approx 1.25 \times 10^{-4} T^2$ W/cm K, is very close to White's estimate. White's estimate of umklapp scattering, based on the high-temperature formula of Leibfried and Schloemann[25] is $K_U = 140/T$ W/cm K. By means of the additive-resistance approximation, $K_g = (1/K_E + 1/K_U)^{-1}$ and is shown by the heavy dashed line in Fig. 6. At low temperatures this estimate is very close to K_g of the 9.35-Mo sample; but the maximum is much too high in magnitude and temperature. Either the estimated umklapp processes are too weak or point-defect scattering reduces K_g of the 9.35-Mo s sample by an order of magnitude at high temperatures.

In order to investigate the effects of point-defect scattering, we make use of the integral formula[2,26,27]

$$K_g = K_0 T^3 \int_0^{\Theta/T} \frac{\tau y^4 e^y}{(e^y - 1)^2}\, dy\,, \tag{22}$$

$$y = \frac{\hbar\omega}{kT}\,,$$

$$K_0 = \frac{k^4}{2\pi^3 v \hbar^3} = 3.6 \times 10^3 \text{ W cm}^{-1}\text{sec}^{-1}\text{K}^{-4}\,,$$

where $\hbar$ is Planck's constant, k is Boltzmann's constant, and ω is the phonon frequency. The Debye temperature Θ of these alloys is listed in Table I. Their average is 570 K, and the sound velocity can be estimated from

$$v = \frac{k\Theta}{h}\left(\frac{V_0}{6\pi^2}\right)^{1/3} = 4400 \text{ m/sec},$$

where V_0 is the volume per atom. The effective relaxation time τ is found from

$$\frac{1}{\tau} + \frac{1}{\tau_E} + \frac{1}{\tau_P} + \frac{1}{\tau_U} + \cdots\,, \tag{23}$$

where the E, P, and U subscripts refer to scattering of phonons by electrons, point defects, and umklapp processes, respectively. There may be other contributions to Eq. (23) such as phonon-magnon scattering, but we shall limit our discussion to these three kinds. For phonon-electron scattering,[2,28]

$$\frac{1}{\tau_E} = \frac{2C^2 h a^3}{9\pi M} k_\xi^2 \left(\frac{dE}{dk}\right)_\xi^{-2} q = F_E\,\omega\,, \tag{24}$$

where a is the lattice parameter, M is the mass of an atom, q is the phonon wave vector, k is—here only—the electronic wave vector, E is the electron energy, and ξ is the Fermi energy. A spherical Fermi surface is assumed. The parameter C is the electron-phonon coupling constant, which is roughly equal to the Fermi energy on the basis of the simplest assumptions.[29] The Fermi energy measured from the bottom of the d band in Cr is about 4.1 eV.[29] Experimentally we find that for 4.57 V and 9.35 Mo, $C \approx 4.1$ eV; for 3.89 Mo, $C \approx 3.7$ eV. Equation (24) leads to $K_g \propto T^2$ at the lowest temperatures.

Point-defect scattering is estimated from

$$\frac{1}{\tau_P} = \frac{V_0 \epsilon}{4\pi v^3}\,\omega^4 = F_P\,\omega^4\,, \tag{25}$$

where ϵ depends on the impurity-mass difference,

$$\epsilon = \sum_{i=1}^{r} \left(\frac{M_a - M_i}{M_i}\right)^2 f_i\,,$$

$$\frac{1}{M_a} = \sum_{i=1}^{r} \frac{f_i}{M_i}\,.$$

The subscript i refers to one of r different mass species, and f is concentration. The constant F_p is listed in Table I.

The umklapp relaxation time is[30]

$$\frac{1}{\tau_U} = 2\gamma^2 \frac{kT}{Mv^2}\frac{\omega^2}{\omega_D} = F_U T \omega^2\,, \tag{26}$$

where ω_D is the Debye frequency, and γ is the Grüneisen constant ($\gamma \approx 2$). Equation (26) leads to $K_g \propto \Theta^3$ at high temperatures ($\Theta \propto \omega_D \propto v$; the integral in Eq. (22) is proportional to Θ/T at high tem-

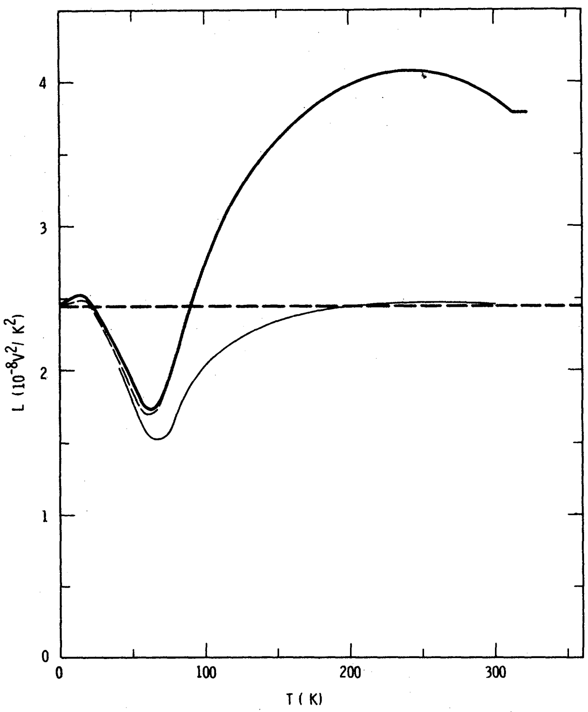

FIG. 7. Lorenz ratio of pure Cr. The heavy dashed horizontal line is L_0. The heavy, solid curve is experimental. Below 312 K, the data are from Ref. 5; and above 312 K, data from Ref. 1 are used. The thin solid curve shows the effect of subtracting off the theoretically estimated lattice thermal conductivity (the heavy dashed line in Fig. 6). The thin, dashed line shows the effect of the experimental lattice thermal conductivity (9.35-Mo sample in Fig. 6). The anomalously high L above 100 K arises from band-structure effects (Refs. 5 and 6).

peratures). The Debye temperature decreases about 6% in the alloy-concentration range considered here. This would lead to about a 20% decrease in K_g, the opposite of the trend that is observed in Fig. 7.

The thin dashed line in Fig. 6 is K_g calculated with Eq. (22) with phonon-electron and umklapp scattering, the only processes expected in pure Cr. The difference between the heavy dashed line and the thin dashed line is the failure of the additive-resistance approximation. When the point-defect scattering calculated for 9.35 Mo is added, the thin dashed line is moved down to the dotted line. Since point-defect scattering is weaker in 3.89 Mo and negligible in 4.57 V on the basis of the mass defect, we conclude that the combination of theoretically estimated umklapp processes and point-defect scattering is not enough to produce a maximum in K_g at the low temperatures where it is observed in the alloys. Furthermore, we do not expect K_g to be larger in pure Cr than is reported here in the 9.35-Mo alloy because of the trend of the data, i.e., the stronger the antiferromagnetism, the smaller is K_g.

Thus, we can only speculate about the reason that theoretical calculation does not fit the data closer.

(a) Umklapp processes are much stronger than the theoretical estimate.

(b) There are strong normal processes which we have not taken account of.[2,31]

(c) Phonon-magnon scattering may be partly responsible for the reduction of K_g of 3.89 Mo below 9.35 Mo and 4.57 V, and may by implication exist in pure Cr.

VI. DISCUSSION OF LORENZ NUMBER

The Lorenz number L of pure Cr (sample Cr 2 in Ref. 5) is shown in Fig. 7 by the heavy solid curve. Above 100 K, L is much larger than the theoretical value L_0 shown by the heavy dashed horizontal line. As was pointed out in Sec. I, the difference has been attributed[2-4] to K_g; that is, $L - L_0 = K_g(\rho/T)$. This explanation appears reasonable if one assumes that K_g(Cr) has the theoretical values given by the dashed line in Fig. 6 obtained by using Cu theory with scaled parameters, for then the corrected values of L given by the thin line in Fig. 7 approach L_0. However, the measured values of K_g shown for the alloys in Fig. 6 imply that K_g(Cr) is even lower than that determined for Cr 3.89 Mo or as much as an order of magnitude lower than the theoretical estimate. Even if the values for Cr 9.35 Mo are used as an upper bound on K_g, their effect on L is negligible at these temperatures. Their only effect is given by the thin dashed line at the lower temperatures. Therefore, we conclude that the large values of $L - L_0$ found in pure Cr at temperatures above 100 K are not caused by lattice thermal conduction. On the other hand, band-structure effects and the opening of the antiferromagnetic energy gap over part of the Fermi surface of Cr at temperatures below T_N can account quite well for details of L's observed behavior.[5,6]

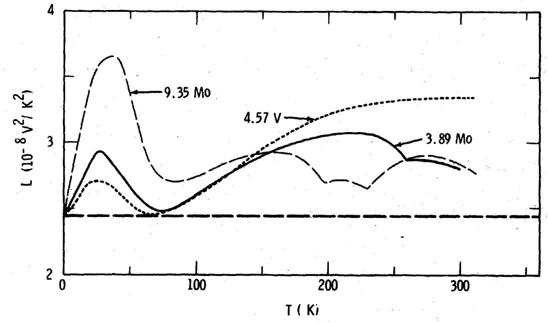

FIG. 8. Lorenz ratio of the alloys. The heavy dashed horizontal line is L_0. The peak below 100 K in the three alloy curves is the effect of K_g. Above 100 K, the anomalously large L is believed to result from a combination of band structure and scattering effects. Relative minima in L exist at T_N in the two Cr–Mo specimens (197 K for 9.35 Mo and 260 K for 3.89 Mo). The second minimum in 9.35 Mo at 230 K is not understood.

The Lorenz ratio of the three alloys is plotted in Fig. 8. Between about 80 K and T_N both antiferromagnetic alloys have a maximum which is similar to the maximum in pure Cr and which we believe arises from the same magnetic-band-structure effects. The maximum in L around 30 K is produced by K_g, and there is a minimum at T_N in both Cr-Mo alloys. In the case of 9.35 Mo, there is another minimum about 30 K above T_N, which is not understood. The L of paramagnetic 4.57 V is different—it rises monotonically from 100 K as Goff's model predicts for pure Cr in the paramagnetic case.[5,6] As in pure Cr, the large $L - L_0$ above 100 K is thought to be an electronic-band-structure effect; but we have not yet attacked the problem quantitatively because of the complications introduced by the additional scattering processes in the alloys.

VII. CONCLUSION

We have presented thermal-conductivity and electrical-resistivity data on three Cr alloys with 3.89 and 9.35-at.% Mo, and 4.57-at.% V, respectively, in the temperature range 3–300 K. K_g has been separated from K, and it is possible to draw several conclusions.

(i) K_g in pure Cr is smaller than previous theoretical estimates.[1,2]

(ii) There is a trend in antiferromagnetic Cr-Mo for K_g to increase with increasing Mo concentration, while T_N is simultaneously decreasing. This trend is suggestive of a phonon-magnon scattering process which is weakened by the addition of Mo impurities. The lattice conductivity of paramagnetic 4.57 V corroborates this trend.

(iii) K_g is too small to cause the anomalously high high Lorenz ratio of pure Cr above 100 K. We believe the anomaly results from the non-free-electron band structure of Cr.[5,6]

(iv) The three alloys studied here also have anomalously high Lorenz ratios above 100 K, but they are lower than in pure Cr. Band structure is thought to cause the anomaly in the alloys also, but the analysis used previously for pure Cr[5,6] is complicated by the existence of additional scattering processes.

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