

Deviations from linear temperature dependence of the electrical resistivity of V-Cr and Ta-W alloys

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Measurements of the electrical resistivity as a function of temperature have been made on a series of bcc V-Cr solid solutions over the range 285 to 1200°K (and at 4.2°K). The deviations from a linear temperature dependence of the resistivity at temperatures higher than the Debye temperature were analyzed in terms of the theory of Mott and Jones, taking into account the change of the Debye temperature owing to thermal expansion. The Debye temperature as a function of alloy concentration is also obtained. Published results on the high-temperature electrical resistivity of Ta-W alloys are also analyzed.

I. INTRODUCTION

The electrical resistivity ρ of a nonmagnetic metal can in general be separated into two components; the ideal resistivity ρ_i and the impurity resistivity ρ_0 ,

$$\rho = \rho_0 + \rho_i. \quad (1)$$

The impurity resistivity can be temperature dependent. For temperatures higher than the Debye characteristic temperature Θ the ideal resistivity can be written¹

$$\rho_i = KT/\Theta^2, \quad T > \Theta, \quad (2)$$

where K is a constant.

Equation (2) is however not strictly obeyed for many metals, and the departures from a linear temperature dependence of the resistivity are particularly marked for transition metals. For transition metals of groups IV and VI, for examples, the resistivity usually increases with temperatures faster than linear; while for transition metals of groups III and V the resistivity increases with temperature more slowly than linear.^{2,3}

According to Mott and Jones⁴ and Ziman,¹ the Debye temperature of a metal should decrease with increasing temperature as the result of lattice thermal expansion,

$$1/\Theta^2 = (1/\Theta_0^2) (1 + 6\alpha\gamma T), \quad (3)$$

where Θ_0 is the Debye temperature at $T=0$ °K. α is the linear coefficient of thermal expansion and γ is the Grüneisen constant. This gives a reasonable explanation of the resistivity deviations for noble metals only and not for most transition metals. In particular, for those transition metals with negative deviations, one must look for other mechanisms.

A second mechanism resulting in the resistivity deviating from a linear temperature dependence was also suggested by Mott and Jones.^{4,5} According to their theory, the conduction electrons in transition metals have wave functions derived

from s and p states just as in Cu, Ag, and Au. However, the resistivity is thought to be determined mainly by scattering processes in which the conduction electrons make transitions to the unoccupied d states under the influence of lattice vibrations. The probability of such process is proportional to the density of states $\nu(\epsilon_F)$ and its derivatives with respect to the electron energy ϵ in the d band at the Fermi level ϵ_F . Therefore, the ideal resistivity can be written, taking into account the Debye temperature effect as given by Eq. (3),

$$\rho_i = (K/\Theta_0^2) T (1 + 6\alpha\gamma T) (1 - AT^2), \quad T > \Theta, \quad (4)$$

where

$$A = \frac{1}{6}(\pi k)^2 \left[3 \left(\frac{1}{\nu} \frac{d\nu}{d\epsilon} \right)^2 - \frac{1}{\nu} \frac{d^2\nu}{d\epsilon^2} \right]_{\epsilon_F}; \quad (5)$$

k is the Boltzman constant.

For transition metals with Fermi energy ϵ_F near a maximum position of the density-of-states curve $\nu(\epsilon_F)$, the first term in Eq. (5) is small compared with the second term, and A will be positive. Accordingly, from Eq. (4) one can expect a negative deviation. On the other hand, for a transition metal with Fermi energy near a minimum of the density-of-states curve, the resistivity-versus-temperature curve is expected to deviate positively.

Shimizu and co-workers,^{3,6} have demonstrated that this simple model agrees well with experimental results for most pure transition metals. In their calculations they made use of ν determined in the rigid-band model from the low-temperature specific-heat data. The purpose of this work is to test this simple model in the case of alloy systems.

The main advantage of studying alloys is that by controlling the alloy concentration, one can obtain a continuous variation of the density of states and the position of Fermi energy. The V-Cr alloy system was chosen for this purpose because of the following reasons: (i) V-Cr forms a continuous solid solution of *bcc* lattice. (ii) There are no

TABLE I. Impurity contents.

Impurity element	ppm in Cr	ppm in V
C	0.01	87
H ₂	0.2	1.4
O ₂	12	10
N ₂	0.9	N. D.
Al	0.3	50
Cu	0.1	2
Fe	12	30
Mg	0.1	1
Mn	0.1	0.3
Ni	0.3	1.0
Si	10	500
Ti	N. D.	5
Nb	N. D.	30
W	N. D.	30
Zr	63	6
Ca	0.3	0.6
P	0.3	10
S	1.7	6

complications due to phase changes in the temperatures of interest. (iii) V and Cr are close neighbors in the periodic table, and most chemical properties change slowly and smoothly on alloying them. In the later discussions, the constant K in Eq. (2) will be assumed to be approximately the same for all alloys. (iv) The Fermi energy of V is near a maximum of the density-of-states curve, while that of Cr is near a minimum. The values of ϵ_F and $\nu(\epsilon_F)$ for V-Cr alloys are the best established among the transition-metal alloys.

The high-temperature electrical resistivity of Ta-W alloy system has been reported by Thomas.⁷ The results are very similar to those of V-Cr. Therefore, we also analyze the Ta-W together with the V-Cr alloys. This provides support to the conclusions one draws from the analysis of V-Cr. Ta and W have, respectively, similar electronic structures as V and Cr.⁸ It is therefore well justified to consider them together.

II. EXPERIMENTAL PROCEDURE

The pure metals, V and Cr, used in this work for the alloy preparation are supplied by Materials Research Corp. The impurity content provided by MRC are listed in Table I. The major impurity is 500 ppm of Si in V.

The alloy samples originate from two sources:

(i) The first set, including $V_{0.77}Cr_{0.23}$, $V_{0.50}Cr_{0.50}$, and $V_{0.05}Cr_{0.95}$, was kindly donated by Schroder. They are the same alloys Schroder and co-workers⁹ used in their study of electrical resistivity. (ii) The second set, including $V_{0.86}Cr_{0.14}$ and $V_{0.70}Cr_{0.30}$, were prepared at Dalhousie University by levitation technique.¹⁰

The concentrations of alloys were obtained from a scanning electron microprobe analysis, and the results are listed in Table II, together with the values estimated from the weights of the component pure metals actually used in the preparation. The two sets of values are seen to be the same. All alloys were tested for homogeneity by scanning and in all cases no inhomogeneity was detected.

The samples were all spark-erosion cut from alloy ingots using bare copper wire. The finished sample surfaces show a roughness of about 2μ . The sample dimensions are about $1 \times 1 \text{ mm} \times 3 \text{ cm}$. Before measurement, each sample was chemically etched and annealed at 1200°C in vacuum (5×10^{-6} Torr) for 48 h. Pure molybdenum wires were used for both current and potential leads, and they were spot welded to the sample. For the resistance measurement a standard four-probe technique was used. A potentiometer with an accuracy of $1 \mu\text{V}$ and a sensitivity of $0.1 \mu\text{V}$ was used to measure both the current and the potential. Sample currents of 100 or 200 mA were provided by a power supply with a stability of 1 part in 10^4 . The electrical resistivity thus obtained has an absolute accuracy of 2%, which is mainly determined by the geometric factor, and a relative accuracy of 0.1%.

A Materials Research Vaseal Furnace was used to vary the sample temperature. It provides an automatically controlled temperature range of $0-1200^\circ\text{C}$ and a uniform-temperature zone 2 in. in diameter and 6 in. in length. The sample was always positioned transversely at the center of the furnace tube in order to minimize the temperature gradients. A calibrated chromel-alumel thermocouple with an accuracy of 0.2°C was used to detect the sample temperature. It was attached to the sample holder. The sample temperature was always stabilized to within 0.05°C during the period of taking readings. Measurements were made with the sample in vacuum ($\approx 5 \times 10^{-6}$ Torr).

For the measurement of residual resistivity, a sample dipstick that could be easily inserted into a

TABLE II. V-Cr alloy concentration.

Alloy	at. % Cr ^a	Standard deviations	at. % Cr ^b
$V_{0.86}Cr_{0.14}$	13.8	0.3	13.7
$V_{0.77}Cr_{0.23}$	22.5	0.8	22.8
$V_{0.70}Cr_{0.30}$	30.1	0.9	30.1
$V_{0.50}Cr_{0.50}$	50.8	1.0	50.4
$V_{0.10}Cr_{0.90}$	90.6	1.3	90.3
$V_{0.05}Cr_{0.95}$	95.2	1.3	95.4

^aFrom electron microprobe analysis by Research and Productivity Council, Fredericton, New Brunswick, Canada.

^bEstimated from the weights of components used in preparation.

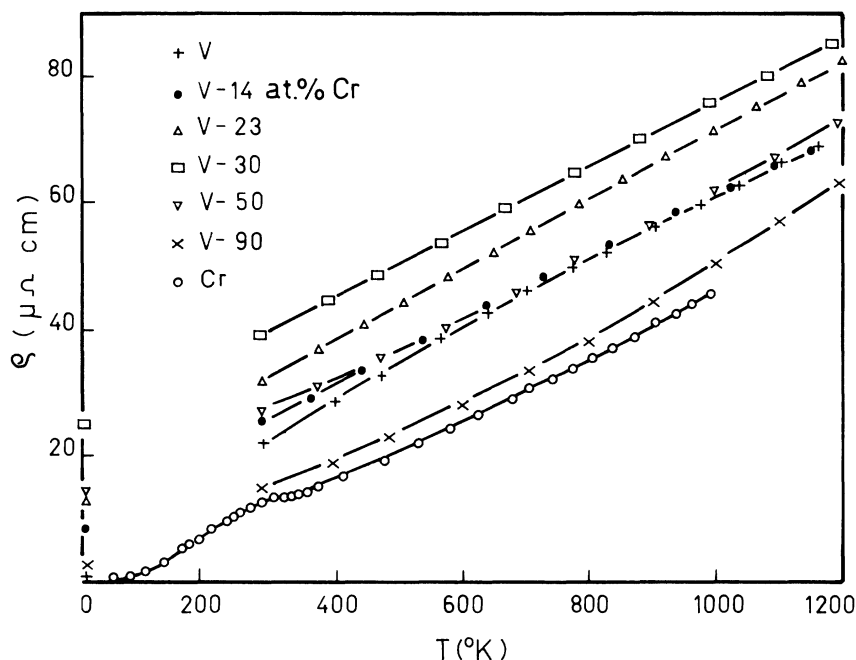


FIG. 1. Electrical resistivity ρ of V-Cr alloys as function of temperature.

liquid-helium Dewar was used. For the measurements at 4.2 °K the samples were slowly lowered into the liquid helium, and subsequently those samples with superconducting transition temperatures above 4.2 °K were slowly raised above the helium until they become normal.

III. RESULTS AND DISCUSSION

The observed electrical resistivity ρ to be discussed in the following has been corrected for the geometrical changes, due to thermal expansion, through the expression

$$\rho = (wt/l)_{299} (1 + \alpha T) R, \quad (6)$$

where w , t , and l are, respectively, the width, thickness, and length of the sample measured at 299 °K. R is the measured resistance. Values of α , the linear thermal-expansion coefficient which is also temperature dependent, were obtained from the published data by L'vov² for V, from the AIP Handbook¹¹ for Cr, and from Conway and Losekamp¹² for Ta and W. For V-Cr and Ta-W alloys, values of α were approximated by linearly interpolating from the values for pure metals.

Figure 1 shows the observed electrical resistivity of V-Cr alloys as a function of temperature. For each sample two runs were made both while increasing the temperature. The maximum difference between two runs on the same sample was observed to be less than 0.5%. Therefore, only the data points of one run are presented for each sample. It is to be noticed that the curves of resistivity vs temperature for V-Cr alloys containing less

than 30-at. % Cr are concave downwards, while those for alloys with higher Cr contents are concave upwards. Only the alloy $V_{0.70}Cr_{0.30}$ appears to show a simple straight line between about 285 and 1200 °K.

Since the temperature dependence of the impurity resistivity is not known, and it is presumably small compared to the deviations from linear behavior in ρ_i which are being studied, we will approximate the impurity resistivity ρ_0 by the observed residual resistivity. Figure 2 shows the results when the residual resistivity ρ_0 is subtracted from the total observed resistivity ρ . The curves now appear to be more systematic than those in Fig. 1. One sees that $\rho - \rho_0$ of pure V is largest among all samples at all temperatures, while that of pure Cr is smallest. The resistivities of V and Cr at temperatures below 285 °K are also included.^{10,13} Pure Cr undergoes a paramagnetic-antiferromagnetic transition at 311 °K. This gives rise to an enhanced resistivity in the antiferromagnetic state. The paramagnetic resistivity, i. e., assuming Cr were not antiferromagnetic below 311 °K, as derived by Chiu *et al.*,¹⁰ is also shown in the figure. In the following analysis, no considerations will be taken on the "precursor effect"¹⁰ on pure Cr and dilute Cr alloys, as this will not introduce significant errors at the end. Pure V is also known to have a transition at 226 °K, but the effect of this transition on the electrical resistivity of V is much less pronounced than in the case of pure Cr,¹⁴ and has been often ignored.

Figure 3 shows the resistivity ρ as a function of

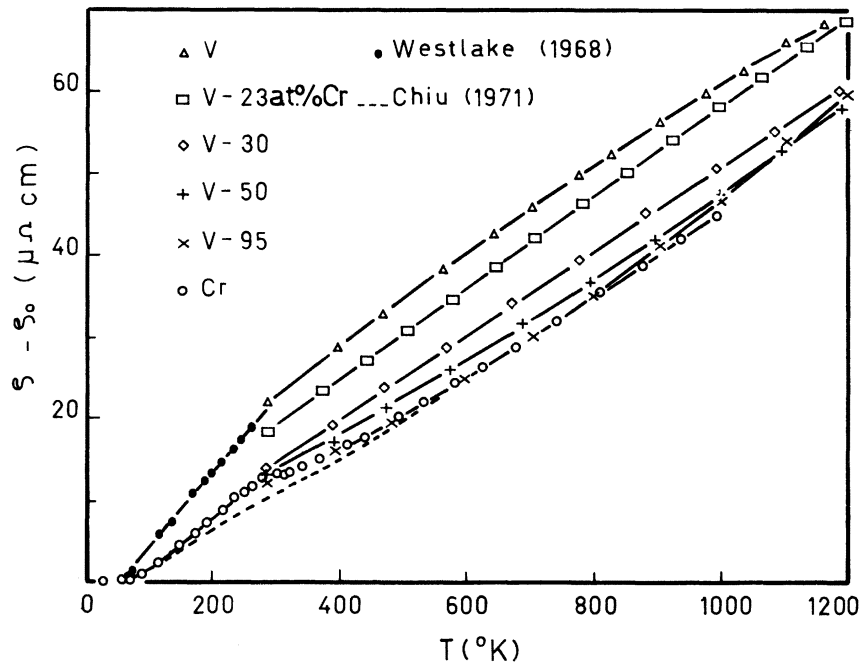


FIG. 2. Electrical resistivity of V-Cr alloys minus residual resistivity, $\rho - \rho_0$, as a function of temperature.

Cr content at different temperatures. A similar plot was also made for the published data on Ta-W by Thomas,⁷ and the results are shown in Fig. 4. The residual resistivities of Ta-W are not available and are estimated in the following way: By noticing

the close similarity between the resistivities of the two alloy systems, we extrapolate the linear ρ -vs- T curve of $\text{Ta}_{0.60}\text{W}_{0.40}$, down to 4.2 $^{\circ}\text{K}$ and use this projected value as the ρ_0 for this alloy (similar to the resistivity of $\text{V}_{0.70}\text{Cr}_{0.30}$). A curve of ρ_0 -vs-

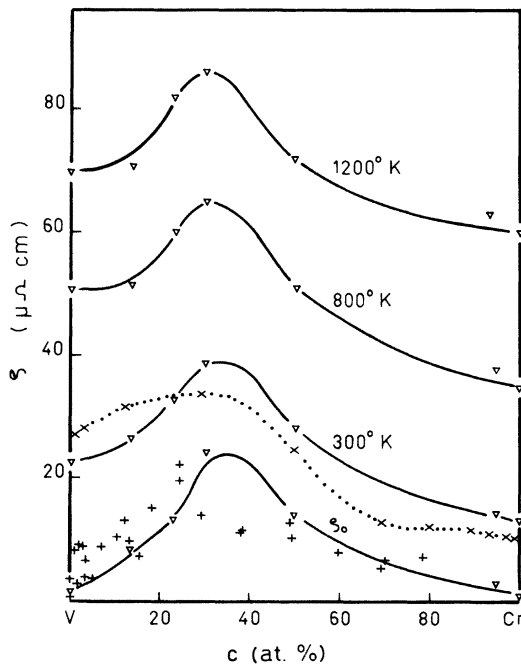


FIG. 3. Electrical resistivity ρ of V-Cr alloys as function of Cr concentration. $+$, Taylor *et al.* at 20 $^{\circ}\text{K}$; \times , Verdernikov at 298 $^{\circ}\text{K}$; ∇ , this work.

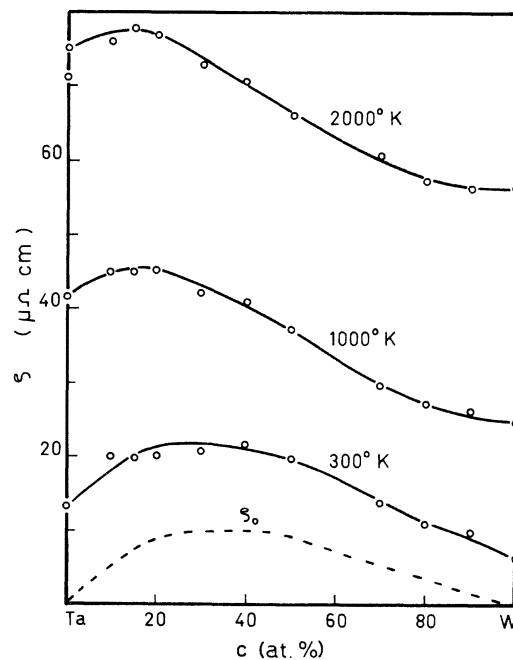


FIG. 4. Electrical resistivity ρ of Ta-W alloys as function of W concentration.

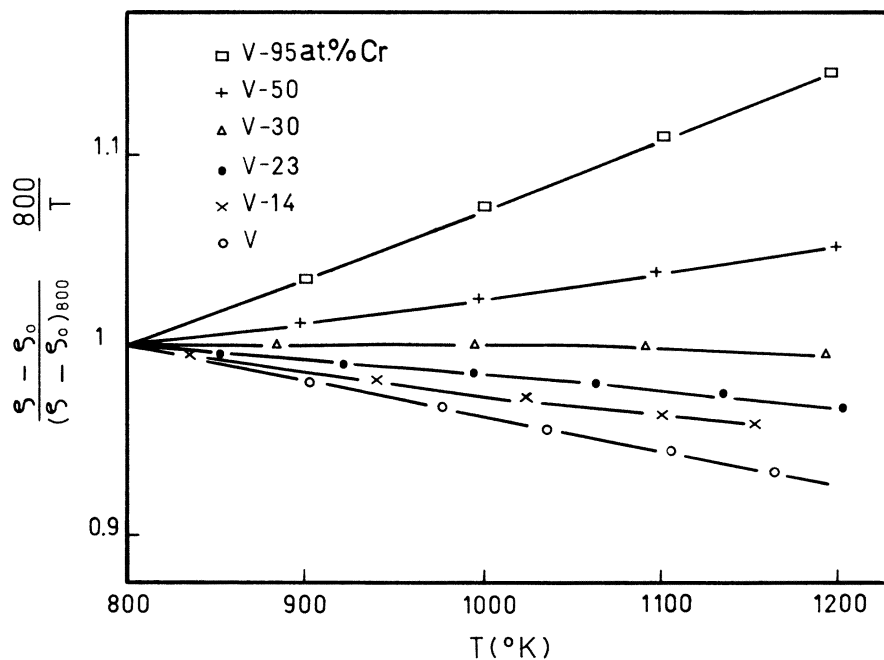


FIG. 5. ρ_i/T of V-Cr alloys normalized at 800 °K as function of temperature.

W content is then drawn such that its shape is similar to other ρ -vs- W concentration curves at higher temperatures. It is to be noticed that for both alloy systems the maxima of the curves do not occur at 50 at. %, and the position of the maximum appears to shift to lower concentrations as the temperature is increased. This is different from what one would expect for a simple solid solution, such as Ag-Au, in which the resistivity can be expressed

as const. $x(1-x)$, where x is the concentration of either component metal,⁴ with the resistivity peaking near $x=50$ at. %. In Fig. 3, the published data by Taylor *et al.*¹⁴ at 20 °K and by Verdernikov¹⁵ at 298 °K are also included for comparison.

In order to best demonstrate the deviations from a linear temperature dependence of the observed resistivity, we have plotted $\chi \equiv (\rho_i/T) (T/\rho_i)_{800}$ vs T for both alloy systems and shown in Figs. 5 and 6.

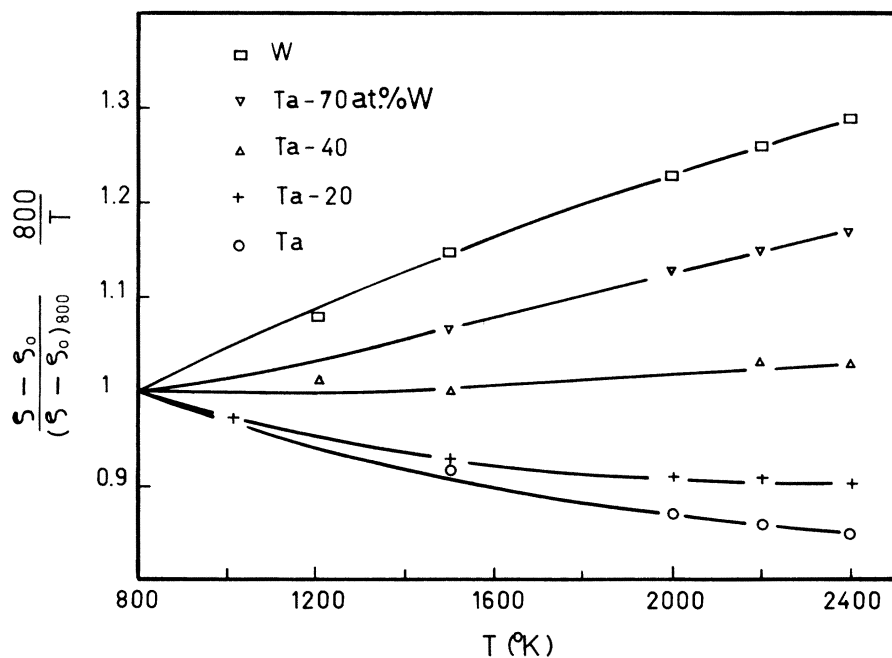


FIG. 6. ρ_i/T of Ta-W alloys normalized at 800 °K as function of temperature.

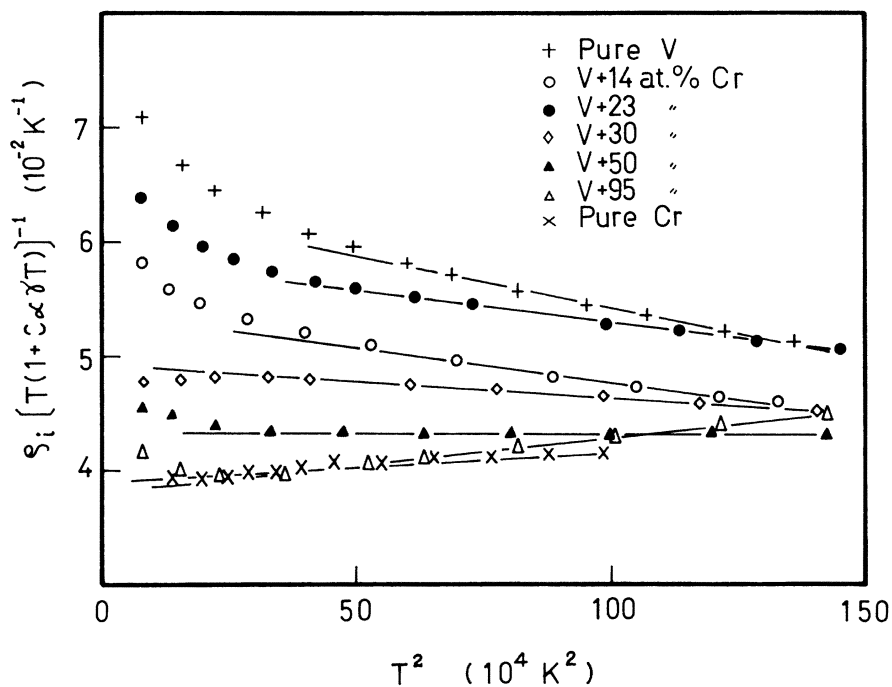


FIG. 7. $\rho_i [T(1+6\alpha\gamma T)]^{-1}$ vs T^2 of V-Cr alloys.

The normalizing temperature of 800 °K safely satisfies the condition of $T > \Theta$ for Eq. (2). If the resistivity is indeed a perfectly linear function of temperature, one will expect χ to be unity for all temperatures. This was observed for $V_{0.70}Cr_{0.30}$ and $Ta_{0.60}W_{0.40}$. For alloys with positive deviations, χ will be larger than unity, and for alloys

with negative deviations, χ will be smaller than unity.

Now, in order to test the theory of Mott and Jones as presented in the form of Eqs. (4) and (5), we analyze the experimental data as follows: (i) The variation of the Debye temperature as shown in Eq. (3) is assumed to be correct. (ii) The data

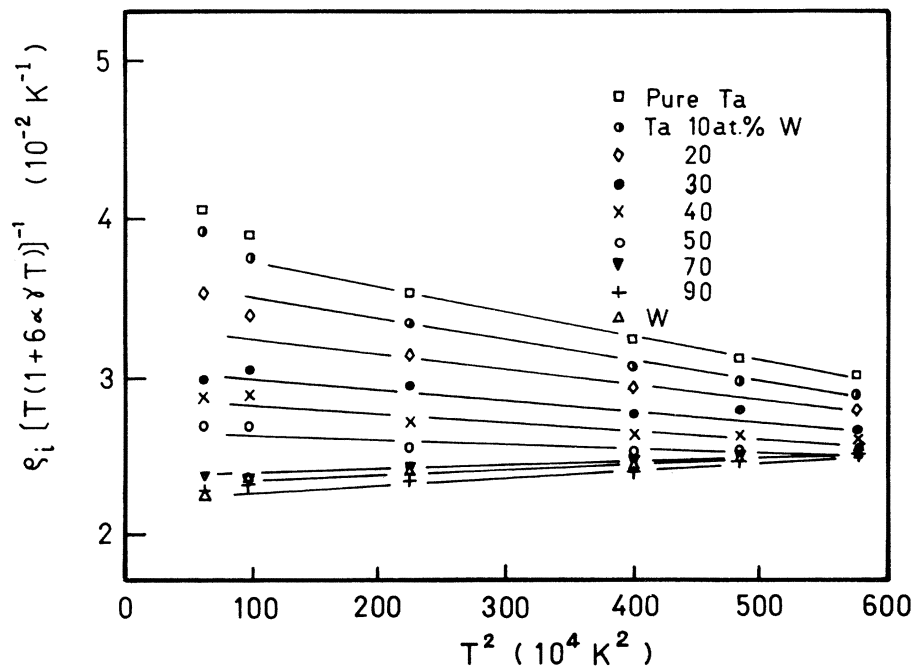


FIG. 8. $\rho_i [T(1+6\alpha\gamma T)]^{-1}$ vs T^2 of Ta-W alloys.

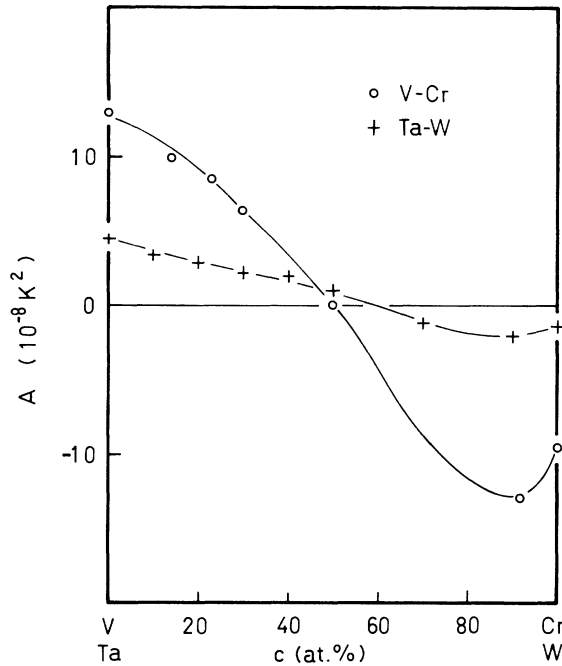


FIG. 9. Coefficient A of V-Cr and Ta-W alloys as function of concentrations.

is then plotted as $\rho_i [T(1+6\alpha\gamma T)]^{-1}$ vs T^2 . If the data fits Eq. (4), one would expect a straight line for each alloy, from which the values of A and K/Θ_0^2 can be calculated. (iii) From Eq. (5) one can also calculate independently the value of A from a known density of state.

Figures 7 and 8 show such plots for V-Cr and Ta-W alloys, respectively, taking $\gamma=1.54$ for V-Cr and $\gamma=1.8$ for Ta-W alloys.¹⁶ It is seen that for V-Cr alloys the results are indeed linear except at temperatures near the Debye temperature, where Eq. (4) is no longer valid. For Ta-W alloys, however, deviations from a straight line appear to persist up to rather high temperatures (~ 1000 °K), which is much higher than the Debye temperature. In such cases, values of A and K/Θ_0^2 are evaluated at temperatures higher than 1000 °K. We therefore can say that Eq. (4) describes reasonably well the observed electrical resistivities of V-Cr and Ta-W alloys for temperatures higher than the Debye temperatures. This suggests that the higher-order term T^4 , which is omitted in Eq. (4), is negligible compared with the AT^2 term.

The values of A as evaluated above are shown in Fig. 9. It is noticed that both alloys systems show similar concentration dependence of the coefficient A . Shimizu¹⁷ has calculated the values of A using the empirical density of states³ obtained from low-temperature specific-heat measurements. Their results for both V-Cr and Ta-W alloys appear to be much larger those shown in Fig. 9. The source

of this discrepancy is not understood. It may suggest a breakdown of the rigid-band model for the alloys. It is then suggested¹⁷ that the density of states of these alloys to be employed in Eq. (5) may have to be calculated in a coherent-potential approximation.

Finally, from Figs. 7 and 8 we can also calculate the value of K/Θ_0^2 for each alloy. Then by assuming K to be independent of concentration and knowing Θ_0 for one alloy or one pure component metal, we can calculate Θ_0 as a function of concentration. The results are shown in Fig. 10. They have been normalized to agree best with the values obtained from the low-temperature specific-heat measurements.^{18,19} It is clearly seen that the values of Θ_0 obtained from two different kinds of measurements agree fairly well in the case of Ta-W alloys, while in the case of V-Cr alloys the comparison is difficult at present, because of insufficient data from other sources.

IV. CONCLUSION

It is found that the systematic deviations from a linear temperature dependence of the high-temperature electrical resistivities of V-Cr and Ta-W alloys can be satisfactorily accounted for by taking into considerations two effects: (i) the Debye temperature decreasing with increasing temperature due to lattice thermal expansion; (ii) an effect with a temperature dependence of $(1-AT^2)$, which is presumably dependent on the shape of the electron density-of-states curve and the position of Fermi

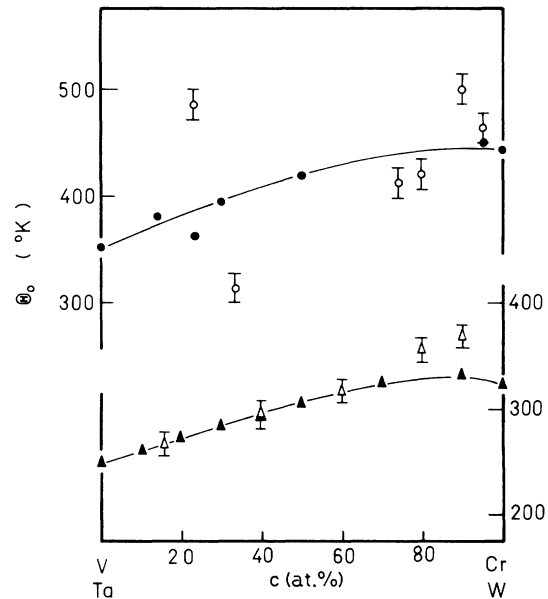


FIG. 10. Debye temperature Θ_0 at $T=0$ °K of V-Cr and Ta-W alloys as function of concentration. For V-Cr: \circ , Cheng, Wei, and Beck, 1960; \bullet , this work. For Ta-W: Δ , Bucher *et al.*, 1965; \blacktriangle , this work.

energy. The discrepancy found between the experimental and theoretical values of A is not understood. It may be due to a breakdown of the rigid-band model, and use of a coherent-potential approximation may give closer agreement. It may be also possible that one should look for a different source, such as the temperature variation of the impurity resistivity. The Debye temperatures at $T=0$ as function of alloy concentration obtained from the high-temperature electrical resistivity agrees reasonably well with the values obtained from the low-temperature specific-

heat measurements.

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