Thermal expansion of chromium at high temperature

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Measurements of linear thermal expansion by pushrod dilatometry to 1873 K confirm the γ-ray density measurements by Stankus in 1993 which indicated that the coefficient of expansion of chromium increases much more rapidly above ~ 1200 K than the heat capacity. The increase in expansion is also much greater than in Mo and W where anharmonicity is important. Magnetic spin effects are a possible source.

I. INTRODUCTION

Chromium has been a topic of interest since Bridgman first observed in 1932 evidence of a phase transition in the electrical resistance near room temperature. This transition was later to be identified by neutron diffraction as a first order antiferromagnetic transition ($T_N = 311$ K). Fawcett[1] in a review of the properties of chromium described it as "... a spin-density wave antiferromagnet *par excellence*. The richness of the phenomena observed in Cr derives from its itinerant SDW (spin density wave), which is a truly many-body effect ..." Most attention has been directed to the physical properties of Cr and dilute alloys near T_N and at low temperatures where magnetoelastic coupling produces marked "anomalies" in the expansion coefficient and elastic moduli. Less attention has been given to the higher-temperature range although it is clear that the anomalies in elastic moduli[2,3] and expansion[4,5] persist up to $T \sim 600$ K. These were shown clearly by comparing values for pure Cr with those for CrV alloys. The addition of a few percent of the neighboring element V suppresses the antiferromagnetism without changing the density or lattice dynamics. Fawcett *et al.*[6] have reviewed the SDW antiferromagnetism in Cr alloys and neutron scattering evidence above the ordering temperature but there remains no general agreement on the nature of the effects which persist above T_N.

There are no elastic moduli (and bulk modulus) measurements above 700 K and a paucity of thermal expansion data above 1000 K. There are data for the heat capacity at constant pressure, C_P, with likely errors of $<2\%$ up to 1600 K and $<5\%$ above this (see assessments by Andersson[7] and Chase *et al.*[8]). These heat capacity data for Cr (and other transition metals) have been compared with computer calculations of the electronic band structure and quasiharmonic lattice entropies by theorists at Los Alamos[9] and Stockholm[10] who each conclude that there are significant anharmonic contributions above 1000 K for Cr, Mo, and W which do not appear in the other transition metals. Further they suggest that Cr may have an additional component at high temperatures, perhaps from spin fluctuations, a view shared by Kaiser and Oleś.[11] Although there are no high-temperature measurements of elastic moduli for solid Cr, there are neutron scattering measurements extending up to 1773 K (Ref. 12) which do not suggest any unusual decrease in phonon frequencies at the higher temperatures.

The present measurements on thermal expansion of Cr were stimulated by observations of Stankus[13] on the density of Cr (and V) at temperatures through the melting point by γ-ray absorption. His results for the volume coefficient $\beta = -d \ln\rho/dT$ gave values of the linear coefficient $\alpha = \beta/3$ for Cr which were much larger than those "provisionally recommended" values in the Center for Information Data Analysis and Synthesis (CINDAS) tables[14] above 1200 K, the coefficient increasing by about 250% from a temperature of $0.5T_m$ to the melting temperature $T_m = 2130$ K. By contrast his values for V agreed with those recommended in the CINDAS tables to within 4%, the coefficient increasing by about 50% from $0.5T_m$ to the melting temperature $T_m = 2170$ K. A 50% increase is similar to that observed for many other cubic transition metals, excepting Mo and W which show a 100% increase over this range. Note that the CINDAS values for Cr were labeled "provisional" because they are a rough mean between widely different sets of expansion data available hitherto above 1200 K.

II. EXPERIMENT

The present measurements of the linear expansion were made in a commercial pushrod dilatometer (Adamel-Lhomargy, Marseille) with an alumina sheath and pushrod in an atmosphere of helium over a temperature range from room temperature up to the limit of 1873 K (1600 °C). The sample was a rod of "ductile" Cr described in earlier work[15] (denoted Cr2) of length 27 mm and diameter 10 mm. The temperature of the rod was measured by a Pt-Rh thermocouple and heated at a rate of 20 K per hour, the length and temperature being recorded every 10 K, during "heating" and "cooling." Calibration of the dilatometer was checked by measuring rods of tungsten (SRM 737) and sapphire (SRM 732) of similar length. The length changes were fitted to a fourth degree polynomial to obtain values $\alpha^* = (1/l_0) \times (dl/dT)$ where $l_0 = 27$ mm. Deviations from the fit were less than 0.3% except below 500 K where the temperature dependence is strongly effected by the transition at 311 K.

After the first heating cycle it was found that some welding occurred above 1700 K between the ends of the sample and the alumina rod. A layer of platinum was evaporated onto the ends of the Cr rod to prevent this welding and the sample rerun to 1873 K. Data obtained in the two heating cycles agreed within 1%. The values registered on cooling agreed well with the heating cycle below about 1500 K but
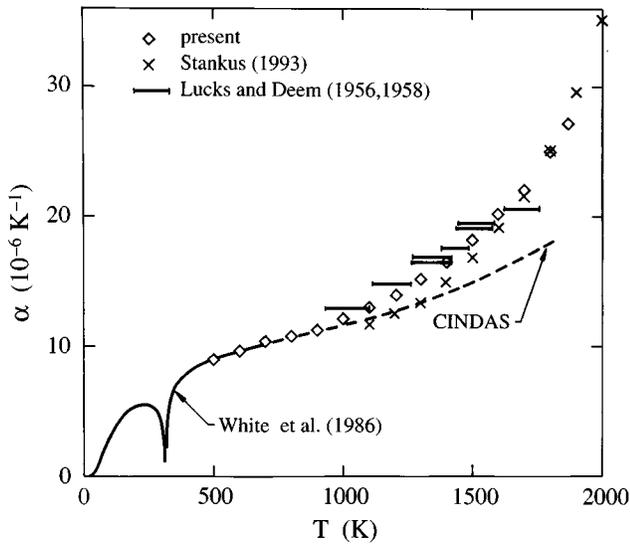
FIG. 1. Linear thermal expansion coefficient $\alpha = d \ln l/dT$ of Cr showing present values ($\diamond$), Stankus ($\times$) (Ref. 13), solid curve (Refs. 4,5), CINDAS (Ref. 14), and earlier x-ray data [Lucks and Deem (Ref. 14)].

differed by 5% at the highest temperature due to the cooling being too rapid for temperature equilibrium in the system. In the ensuing discussion we have used the "heating" cycle data. To compare present data with those of Stankus we convert values of α^* to α using the length changes Δl:

$$\alpha^* = \alpha(1 + \Delta l/l_0).$$

The present results are shown in Fig. 1 together with our earlier interferometric data[4,5] below 800 K, the CINDAS "provisionally recomended" curve and the x-ray values obtained by Lucks and Deem in 1956 and 1958 (see Ref. 14). Agreement with Stankus is satisfactory above 1500 K but his values appear to be low below this.

III. DISCUSSION

The present α values support the data of Stankus obtained by γ-ray absorption and indicate an unusually large increase in the thermal expansion coefficient above about 1200 K. The unusual extent is illustrated in Fig. 2 which compares $\alpha(T)$ as a function of reduced temperature T/T_m for Cr with Mo, W, V, and Pt. Note particularly the comparison with the other group-VIB elements W and Mo. The upper curves in Fig. 2 show the heat capacity at constant pressure, C_P, for Cr and for Mo and W (indistinguishable in this reduced temperature plot).

For both W and Mo, α and C_P increase at high temperature to a rather similar degree so that the Grüneisen ratio

$$\gamma = 3\alpha B_S V/C_P$$

is sensibly constant, with a value of ~ 1.6, up to 70% or 80% of the melting temperature. Earlier analyses of these properties for Cr using the CINDAS "provisional" values of α gave a similar constancy with $\gamma \approx 1.5$.[4,10] These assumed also a linear extrapolation of the bulk modulus above 700 K, i.e., the measured values used of $B_S = 195$ GPa at 600 K,
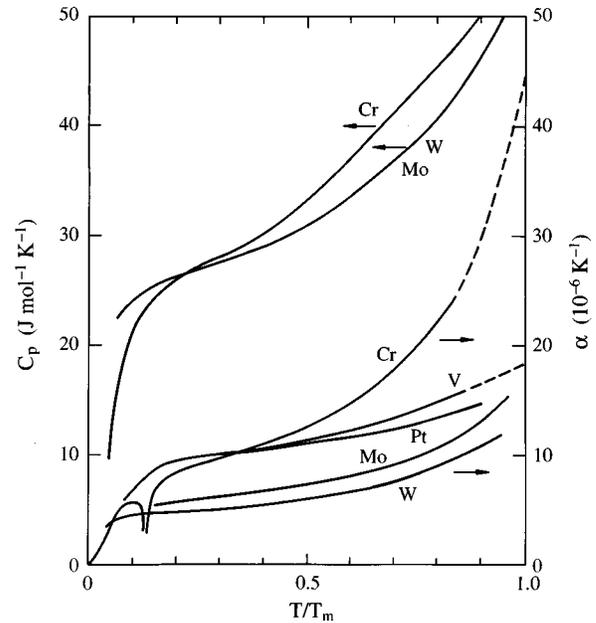
FIG. 2. Variation of α with reduced temperature T/T_m for Cr (melting temperature $T_m = 2130$ K), Mo (2897 K) W (3693 K), V (2170 K), and Pt (2042 K) and C_P for Cr, Mo, and W (upper curves). Dashed curves for α are from Stankus (Ref. 13).

193.5 GPa at 700 K, and a constant slope $dB_S/dT = -0.016$ GPa K^{-1} from Refs. 2, 3, 16.

Using the present expansion data and a similar linear extrapolation for B_S, we obtain values of $\gamma \approx 1.5$ (500–800 K), ≈ 1.6 (800–1200 K), 1.8 (1500 K), 2.1 (1800 K), and 2.7 at 2000 K. However, it is likely that this linear extrapolation, i.e., constant value, of dB_S/dT is inaccurate because of the increasing thermal expansion. The alternative method of extrapolation is to attribute the major change in B_S to a volume change so that $dB_S/dT = B_S\beta\delta_S$ with $\delta_S = d \ln B_S/d \ln V \approx -3.0$. This method (with the present expansion data) gives values of B_S which fall increasingly rapidly above 1200 K to a value of about 157 GPa at 2000 K (compared wih 178 GPa from linear extrapolation). These values, based on a volume change, lead to γ values of about 1.7 (1500 K), 2.0 (1800 K), and 2.5 (2000 K).

Extending the volume extrapolation to the melting temperature 2130 K yields a value of $B_S \approx 147$ GPa which is consistent with the ultrasonic value for liquid Cr of 115 GPa,[17] allowing for the 6% decrease in density on melting.

What can we conclude from the present measurements and those of Stankus? First there is an unusually large increase in the thermal expansion of Cr above ~ 1200 K compared to Mo and W and it may be associated with magnetic spins rather than lattice modes. Grimvall et al.[10] concluded from their analyses of the heat capacity and entropy of Cr compared with W and Mo that the additional contribution at high temperature was probably magnetic and related to spin fluctuations. Note that the increased expansion values will increase the necessary corrections for a volume change in their calculation of the electronic and quasiharmonic contributions.

Another interesting fact emerges from the data taken by Stankus through the melting temperature: For V, the density

decreases by about 4% on melting and the expansion coefficient increases about 50% which seems qualitatively consistent. For Cr, the density also decreases by about 6% but the coefficient of expansion *decreases* nearly 20%, suggestive of the disappearance of a spin contribution.

The interesting behavior of chromium appears to persist to high temperatures. We hope to do expansion measurements on alloys of Cr with 5% and more V when these are available.

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