

THE ANOMALOUS THERMAL EXPANSION OF CHROMIUM

By G. K. WHITE*

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Summary

Experimental data on the linear thermal expansion between 20 and 50 °C of specimens of high-purity chromium confirm the existence of an anomaly centred at 38 °C. The exact shape of this expansion anomaly between about 37 and 39 °C varies markedly from sample to sample, but outside this narrow temperature interval the behaviour is more regular and seemingly related to antiferromagnetic ordering. Data on expansion are compared with other recent observations on heat capacity, magnetic susceptibility, and electrical resistivity of high-purity chromium. It is suggested that an electronic term in the expansion coefficient, observed below 20 °K to be negative, is sensitive to band structure and may be partly responsible for the change in expansion coefficient.

I. INTRODUCTION

The physical properties of chromium between 30 and 40 °C have long been rather puzzling. Sully (1954) has summarized most of the data obtained up to about 1953, usually for samples of rather high impurity content. These data indicated a marked minimum in the expansion coefficient α and in the Young's modulus and a sharp peak in the internal friction at or near 38 °C. A knee-shaped anomaly was observed in the electrical resistivity and Bridgman showed that increase in pressure could reduce the temperature at which this knee occurred by 50 degC or more. No definite anomaly was established in the heat capacity or magnetic susceptibility nor was any change in the body-centred cubic structure of chromium observed.

Due largely to the efforts of Greenaway and others at the Aeronautics Research Laboratory (A.R.L.), Melbourne, quantities of ductile chromium became increasingly available for research investigations after about 1954, and experimental data gathered in the period 1954 to 1959 have been summarized in the review of Edwards, Nish, and Wain (1959). This ductile chromium produced by electrodeposition from suitable solutions has a nitrogen content generally below 0.001 wt.-% (0.003 at.-%) and an oxygen content of 0.04 wt.-% or less. However, the observations on high-purity material have still revealed anomalies in resistivity (for example, Harper *et al.* 1957; de Vries and Rathenau 1957) and elastic moduli (de Vries and Rathenau 1957; Pursey 1958). In addition, Lingelbach (1958) observed a small knee-shaped anomaly in the magnetic

* Division of Physics, C.S.I.R.O., University Grounds, Chippendale, N.S.W.

susceptibility of a ductile chromium sample (from A.R.L.) near 37 °C and Straumanis and Weng (1955) reported a marked change in slope of the expansivity curve from X-ray observations of a sample containing less than 0.02% nitrogen. The latter workers expressed their results in terms of a linear expansion coefficient of $7.47 \times 10^{-6}/\text{degC}$ above 32.5 °C and 4.4×10^{-6} below 32.5 °C (see Fig. 3), although their lattice spacings obtained between 10 and 40 °C might equally indicate a gradual change in coefficient rather than an abrupt change at 32.5 °C. There was no line broadening suggestive of any alteration in the b.c.c. structure.

Further interest and difficulty arose when the first neutron diffraction observations, made on powdered chromium by Shull and Wilkinson (1953), indicated that antiferromagnetic ordering set in below about 175 °C, a temperature well above that at which these other anomalies appear.

Since the review by Edwards, Nish, and Wain was written, some major developments have been as follows.

- (a) Neutron diffraction studies by Bykov *et al.* (1959), Corliss, Hastings, and Weiss (1959), Bacon (1960), and Wilkinson, Wollan, and Koehler (1960) on both single crystals and polycrystals have indicated a Néel point near 39 °C.
- (b) Beaumont, Chihara, and Morrison (1960) have observed a small lambda-shaped anomaly in the specific heat of A.R.L. chromium at about 38 °C.
- (c) Newmann and Stevens (1959) have reported on the magnetic susceptibilities, electrical resistivities, and expansion of alloys of chromium with small quantities of iron.
- (d) Collings, Hedgcock, and Siddiqi (1961) have made further observations on the magnetic susceptibility of A.R.L. chromium, confirming the appearance of a bump at 38.5 °C. They have also studied electron spin resonance in this chromium and in chromium to which chromic oxide has been added; they conclude, like Newmann and Stevens, that the magnetic anomaly is characteristic of pure chromium and is not merely associated with the presence of oxide.
- (e) X-ray observations of lattice spacing by Straumanis and co-workers (personal communication 1960) on samples with very low nitrogen content have led them to believe that an anomaly in the lattice parameter-temperature curve near 33 °C (Straumanis and Weng 1955, and Fig. 3 below) only appears when nitrogen is added to the sample. Apropos of the role which may be played by nitrogen impurity, thermoelectric power measurements of Edwards (personal communication 1960) have continued to show an anomaly when the nitrogen content fell below 0.0004 wt.-%.

The present paper reports some rather sensitive observations of linear thermal expansion of A.R.L. chromium which suggest that an anomaly persists with the purest samples, although the detailed form of the change in expansion coefficient very close to 38 °C may be very sensitive to impurity content or to metallurgical condition.

II. EXPERIMENTAL DETAILS

A detailed description of the apparatus used for measuring linear thermal expansion has been given recently (White 1961a). Briefly, it depends on the comparison of three-terminal capacitors in a bridge with transformer ratio arms (Thompson 1958). A sample, 2 in. long with flat parallel end-faces of $\frac{7}{8}$ in. diameter, is mounted in an Invar cell (Mark I) or a copper cell (Mark II) to form a three-terminal capacitance. The well-defined capacitance between one end-face and the cell is about 5 pF and is determined to an ultimate limit of $\pm 1 \times 10^{-6}$ pF. This allows the change in length of the chromium sample to be determined relative to the change in length of cell. The cell is mounted in a cryostat specifically designed for use from near 100 °K down to 1 °K, where relative changes of 10^{-8} cm may be detected. For the purposes of obtaining data near room temperature on chromium, the cryostat was surrounded by a well-stirred oil bath, the temperature of which was controlled to a constancy of about 0.001 degC, using an electronic controller (Wylie 1948). This controller heats the oil bath electrically in response to a signal from an a.c. Wheatstone bridge, one arm of which is a sensitive copper resistance thermometer mounted in the bath. The actual temperature of the bath was measured by a platinum resistance thermometer.

In order to convert relative length changes of chromium with respect to the expansion cell into absolute values for chromium, the following figures have been used for the expansion coefficient of Invar and of copper between room temperature and 50 °C: 1.2×10^{-6} /degC for Invar and 16.7×10^{-6} /degC for copper. The former value for Invar was obtained by calibrating the cell Mark I with a copper specimen, and the value for copper was obtained from published data (Nix and MacNair 1941; Rubin, Altman, and Johnston 1954).

The chromium samples used were kindly supplied by Dr. H. L. Wain, of the Aeronautics Research Laboratory, Melbourne, and were machined and analysed in that laboratory. In the cases of Cr 1, Cr 2, and Cr 3a, samples were annealed by us at 800 °C for about 4 hr, each being sealed off *in vacuo* in a silica tube. Before measurements were made, the end faces were also lapped to flatness and parallelism of about 10^{-5} in.

Analyses and metallurgical history are as follows:

- Cr 1: machined from extruded bar, 0.0008 wt.-% N₂, 0.03 wt.-% O₂.
- Cr 2: machined from extruded bar, 0.0008 wt.-% N₂, 0.03 wt.-% O₂.
- Cr 3: machined from arc-cast slab which had been press forged at 1050 °C, 0.0004 wt.-% N₂, 0.03 wt.-% O₂.
- Cr 3a: Cr 3 after annealing at 800 °C and relapping.

In the case of Cr 1, which shows the most marked expansion anomaly near 38 °C, and was somewhat discoloured by annealing, re-analysis after completion of measurements showed no *observable* change in impurity content. It should be noted that nitrogen analyses may be in error by ± 0.0004 wt.-%.

The results shown below are compared with measurements of heat capacity C_p (Beaumont, Chihara, and Morrison 1960), magnetic susceptibility (Collings, Hedgcock, and Siddiqi 1961), electrical resistivity ρ (Harper *et al.* 1957), all made on A.R.L. chromium samples: the heat capacity sample showed 0.001 % N₂

and 0.04% O_2 ; one magnetic susceptibility sample showed 0.0004 wt.-% N_2 and probable O_2 content of 0.01–0.04%, and is identical with sample Cr 5 used by Harper *et al.* (see resistivity curve in Fig. 3). A second susceptibility sample of more recent origin is probably of slightly higher purity but gave values lying on the same curve (see Fig. 3).

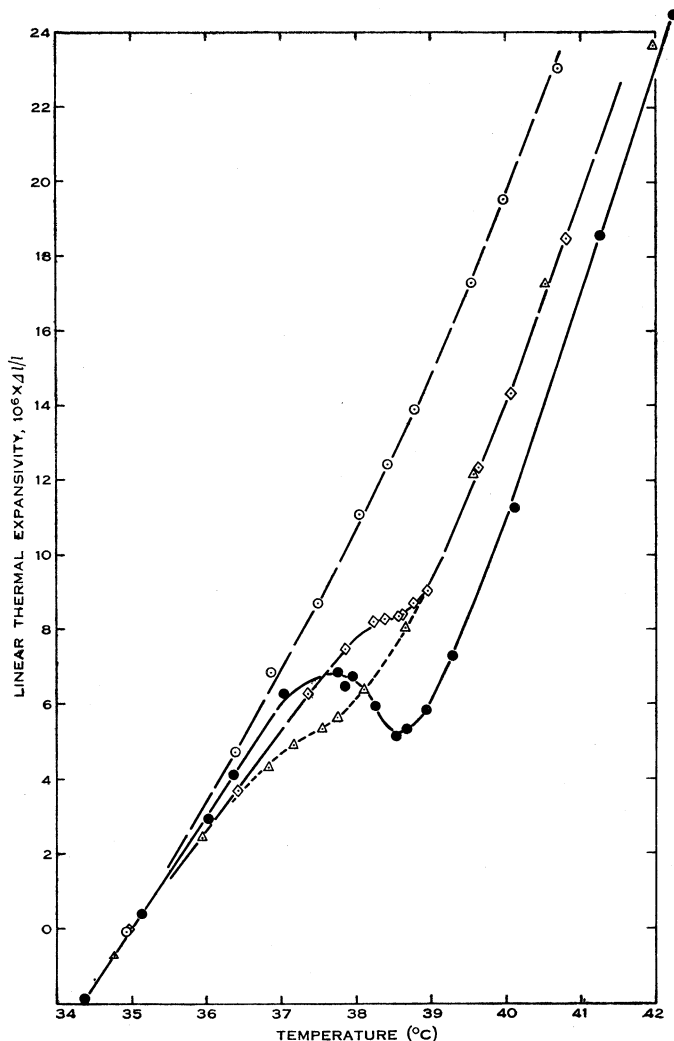


Fig. 1.—Linear thermal expansivity, $\Delta l/l$, of chromium (normalized to zero at 35 °C). ● Cr 1, ◇ Cr 2, ○ Cr 3, △ Cr 3a.

III. RESULTS

In Figure 1 values are plotted of linear thermal expansivity (expansion per unit length) between 34 and 42 °C of the four specimens. Values for Cr 1 were obtained relative to Invar and corrected for the expansion of the Invar, and those for the other three samples were obtained relative to copper and corrected.

For purposes of comparison over this narrow temperature interval, values have been reduced to a common zero at 35 °C.

The slope at each point in Figure 1 represents the coefficient of linear expansion; it can be seen that for each sample the slopes are very similar except in the interval between 36 and 39 °C (see also Fig. 3). Only for Cr 1 is there a minimum in expansivity and hence a negative expansion coefficient. In Figure 2 a full curve is drawn showing the coefficient of expansion α for Cr 1 and Cr 3, determined from the slopes of the expansivity curves in Figure 1. The dashed curve of α below 293 °K (20 °C) is an extrapolation based on length changes observed over the temperature intervals 293–273°, 273–193°, 193–90°, 90–80°, and 80–70 °K. From 25° down to 1 °K, detailed observations on Cr 2, Cr 3, and

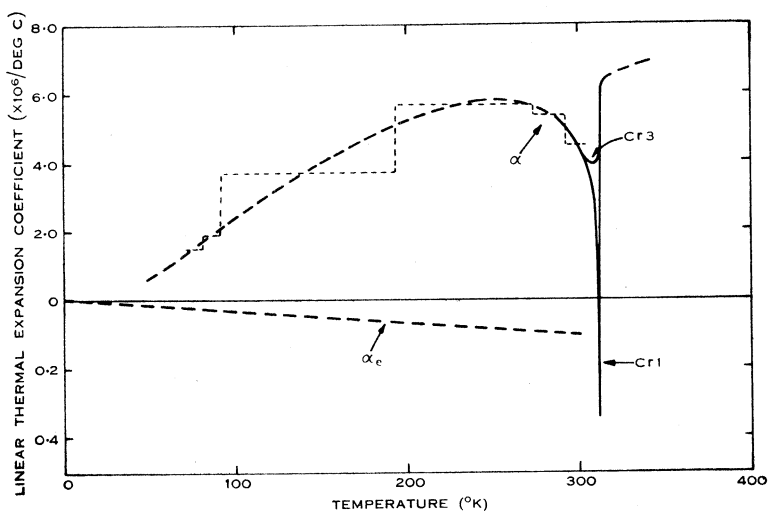


Fig. 2.—Linear thermal expansion coefficient α of chromium. The electronic component α_e is extrapolated from data obtained below 20 °K (White 1961b). The dotted "steps" represent the average expansion coefficients determined over temperature intervals 70–80 °K, 80–90 °K, etc.

Cr 3a have been made and these have yielded a linear expansion coefficient $\alpha = -(35 \pm 4) \times 10^{-10} T$ per degC (White 1961b), which presumably is electronic in origin and, at these low temperatures, much larger than the coefficient arising from the vibrational energy of the lattice, which is expected to vary as T^3 . The dashed line, α_e , represents an extrapolation of this electronic term and indicates that near room temperature the free electrons may contribute a negative term of magnitude about -1×10^{-6} per degC to the linear expansion coefficient.

Our present *relative* expansion cells, either of Invar or of copper, are rather unsuitable for precise studies on chromium between 30 °K and room temperature. It is hoped that soon a new *absolute* expansion cell will be completed and that, if a suitably shaped chromium specimen can be obtained, its expansion coefficient can be measured directly in this temperature range. In the case of Cr 1, some data were obtained for the expansivity between 140 and 170 °K in the Invar cell,

to determine whether any anomaly was obvious in this region, as suggested by the neutron diffraction observations of Bykov *et al.* (1959) which showed that antiferromagnetic ordering disappeared below about 158 °K. We observed nothing unusual in the expansivity curve.

IV. DISCUSSION

Comparison of the expansivity curves in Figure 1 with earlier data on rather impure chromium summarized by Sully (1954) and with that of Newmann and Stevens (1959) on chromium alloys containing small percentages of iron, shows that the form of anomaly—whether in expansivity or in expansion coefficient—is strongly impurity-dependent. Although chemical and gas analyses show no definite difference in purity between our Cr 1 and Cr 2, the former sample exhibited definite discoloration due to annealing, and has a marked minimum in expansivity curve between 38 and 39 °C. It seems probable to the author that the rather smooth curve of Cr 3 is most representative of pure chromium; it is not inconceivable that differences in grain size or preferred orientation contribute to the differences shown in Figure 1, but it seems unlikely. Except in the very narrow temperature region between about 34 and 39 °C, our specimens give rather similar curves of expansion coefficient (Fig. 2), and these in turn are quite similar to that observed by Fine, Greiner, and Ellis (1951; see also Sully, *loc. cit.* p. 80).

Turning to the nature of the anomaly, there is no evidence to suggest the occurrence of any change in crystal structure or lattice rearrangement. Therefore, presumably it is electronic in origin and related to the anomalies occurring in other physical properties at the same temperature, anomalies which are in turn related to the onset of antiferromagnetism. It is tempting to suggest that part of the change in expansion coefficient stems from a change in the magnitude or even sign of the electronic component α_e . It has been shown (for example, Mott and Stevens 1957; Goodenough 1960; Shimizu and Takahashi 1960) that the Fermi energy ε_F in chromium probably lies close to a minimum in the density-of-states curve, the minimum being produced by the narrow overlap of two energy bands. Shimizu and Takahashi suggest that ε_F lies very slightly above the minimum on a steeply rising part of the density-of-states curve. Following Varley's (1956) theoretical treatment of electronic thermal expansion, the rather large positive value of $\partial n(\varepsilon_F)/\partial \varepsilon_F$ which would result from this could lead to a negative value for the electronic expansion term. Then a small change in the band shape or position of ε_F consequent upon the change in magnetic ordering near 38 °C might cause α_e to change appreciably. This need not imply any dramatic change in the actual density of states $n(\varepsilon_F)$ at the Fermi surface, which presumably would raise or lower the heat capacity curve.

Alternatively, an explanation may be sought based on Zener's views (1955) on the exchange interaction between the unfilled electron shells. Chandrasekhar (1958) has applied this concept of repulsive interaction between unfilled shells with parallel spins and attractive interaction between shells with antiparallel spins to explain the expansion anomalies ("knees" in the expansivity curve rather like Cr 1 in Fig. 1 or Fig. 3) observed in the rare earths gadolinium,

terbium, and dysprosium (Barson, Legvold, and Spedding 1957; also Birss 1960 for Gd). This explanation may be satisfactory in the case of Curie points in Gd and Tb but seems less satisfactory for Néel points in Dy and Cr 1.

Figure 3 provides an interesting comparison of the anomalous behaviour in physical properties of chromium. Excepting the curve $\Delta a/a$ (taken from Fig. 2—lattice constant for sintered electrolytic chromium—of Straumanis and Weng 1955), the data were all obtained on samples of A.R.L. chromium of comparable purity. The resistivity anomaly is of rather the same knee-shape as that observed

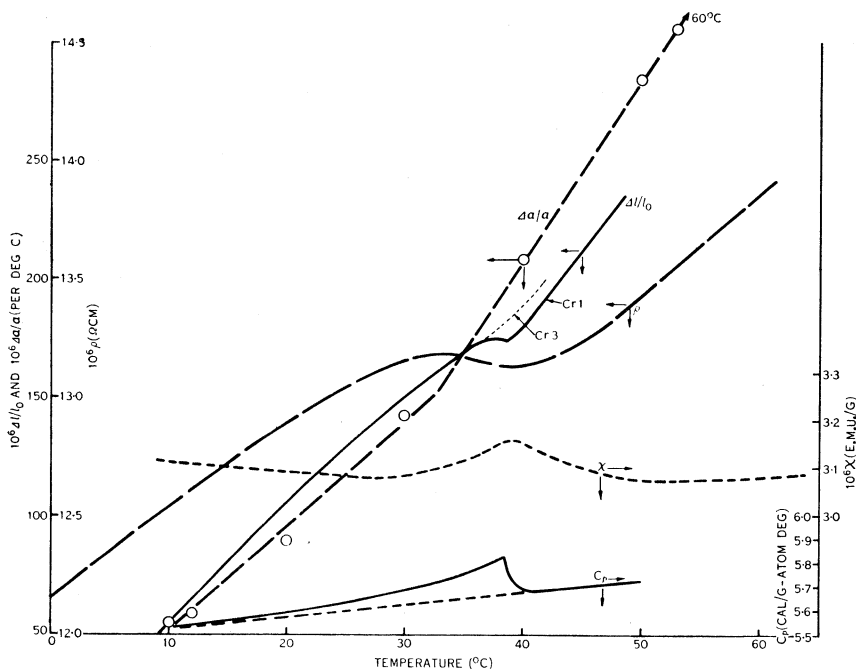


Fig. 3.—Some experimental data for high-purity chromium. $\Delta a/a$: linear expansivity from X-rays (Straumanis and Weng 1955), $\Delta l/l$: linear expansivity of Cr 1 and Cr 3, ρ : electrical resistivity (Harper *et al.* 1957), χ : magnetic susceptibility (Collings, Hedgecock, and Siddiqi 1961), C_p : heat capacity (Beaumont, Chihara, and Morrison 1960).

in some rare earth elements (e.g. Hall, Legvold, and Spedding 1960) and in α -manganese (White and Woods 1957). Coles (1958) has attributed the resistivity anomaly to change in scattering of the conduction electrons by the magnetic spins, the small maximum arising perhaps from increased scattering when only small local regions of spins are ordered. Certainly the neutron diffraction evidence in Cr and Mn indicates that the onset of antiferromagnetism (Néel point) occurs in the vicinity of the shallow minimum rather than at the maximum.

V. CONCLUSIONS

Most recent theoretical speculation on the electronic structure of chromium has been concerned with the evidence afforded by neutron diffraction experiments

and studies of the magnetic susceptibility of chromium and its dilute alloys. Possible patterns for the behaviour of the magnetic spins have been discussed by Corliss, Hastings, and Weiss (1959), Kaplan (1959), Newmann and Stevens (1959), Cooper (1960), Lomer (1960), and Overhauser and Arrott (1960). The evidence presented here for the expansivity of high purity samples supplements the other recent evidence on heat capacity, susceptibility, and thermoelectric power in clarifying the experimental picture. It suggests that very small traces of impurity do influence the expansion anomaly (or "transition") over a very narrow temperature region near the Néel point; but that, disregarding this narrow interval, a genuine change in expansion coefficient occurs which is characteristic of pure chromium and related to the process of antiferromagnetic ordering.

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