

## Anomalies in the Elastic Constants and Thermal Expansion of Chromium Single Crystals

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The temperature dependence of the elastic constants of two single crystals of chromium was investigated from 77 to 500°K. A detailed study was made of the anomalies at the Néel temperature, 310°K, and at the low-temperature transition at 120°K. The magnetic contribution to the elastic constants was found to be significant and to differ, in particular, between the two shear modes,  $c_{44}$  and  $\frac{1}{2}(c_{11}-c_{12})$ . An anomaly in the coefficient of thermal expansion was observed at the Néel temperature.

### I. INTRODUCTION

**A**NOMALIES in the temperature dependence of the elastic properties and of the thermal expansion of metallic chromium have been reported by a number of investigators.<sup>1-5</sup> All of these studies were made on polycrystalline chromium of varying purity and metallographic condition. Even in the highest purity ductile chromium, anomalies were observed in Young's modulus and in the modulus of rigidity at approximately 310 and 120°K; a thermal expansion anomaly was observed only at 310°K.

A preliminary report previously has been given of the investigation of the elastic constants and thermal expansion of single crystals of chromium.<sup>6</sup> The present paper reports in more detail the temperature dependence of the elastic constants and thermal expansion of two single crystals of pure chromium in the temperature range including both high-temperature and low-temperature anomalies: the elastic constants, between 77 and 500°K; the thermal expansion, between 77 and 360°K. The acoustic velocities used to obtain the elastic constants were measured by a high-frequency ultrasonic continuous wave (cw) technique. The thermal expansion of chromium was measured relative to that of fused quartz by means of a dilatometer incorporating a linear variable differential transformer.

The results indicate a marked influence of the antiferromagnetic contributions to the elastic constants. This contribution differs among the compressional constant  $c_{11}$  and the shear constants  $c_{44}$  and  $C' = \frac{1}{2}(c_{11} - c_{12})$ . The shear constants, in particular, show a larger anomaly at 120°K than at 310°K; this behavior is reversed for  $c_{11}$ . Neutron diffraction work<sup>7</sup> on the same chromium crystal is cited as evidence for the anomaly

at 310°K corresponding to a transition from the paramagnetic to an antiferromagnetic state, and for the anomaly at 120°K corresponding to an antiferromagnetic-antiferromagnetic phase transition.

### II. EXPERIMENTAL PROCEDURE

The chromium single crystal was grown by M. J. Marcinkowski from a bar of pure (~99.95%) U. S. Bureau of Mines arc-cast chromium by annealing at a temperature of approximately 1500°C for several hours. The measured impurities in this bar were 10 ppm (parts per million) by weight hydrogen, 50 ppm nitrogen, less than 200 ppm oxygen, and traces of iron and silicon. The crystals were oriented by Laue x-ray back reflection photographs.<sup>8</sup> Two cylindrical crystals, with axes oriented, respectively, along the [100] and [110] crystallographic axis of the cubic crystal, were cut from the original bar. Cutting was done with a diamond metallurgical cutoff wheel under water cooling. Preliminary hand grinding with AO302 alundum on a cast iron lap was followed by etching to a depth of  $5 \times 10^{-3}$  cm. The etchant was a heated solution of 1:1 HCl and H<sub>2</sub>O; rate of etching was approximately  $5 \times 10^{-4}$  cm per min. Final grinding and polishing was done using AO303  $\frac{1}{2}$  alundum on a lead lap, with pure odorless kerosene as lubricant. The finished faces were flat and parallel to within  $6 \times 10^{-5}$  cm. Physical characteristics of the two finished specimens are given in Table I. Lengths were measured with precision gauge blocks and a high-magnification dial gauge to a precision of  $\pm 5 \times 10^{-5}$  cm. The room-temperature density used was the theoretical density obtained from the known atomic weight<sup>9</sup>  $M = 52.01$  and from unit cell dimensions

TABLE I. Physical properties of chromium single-crystal specimens.

	Orientation	Length <sup>a</sup> (cm)	Diameter (cm)	Density <sup>b</sup> (g/cc)
Cr No. 1	[100]±0.5°	0.34956	0.48	7.200
Cr No. 2	[110]±0.5°	0.20856	0.48	7.200

<sup>a</sup> Measured at 24°C.

<sup>b</sup> Calculated from lattice constants at 25°C.

<sup>8</sup> We are indebted to Dr. A. Taylor and Brenda Kagle for these photographs.

<sup>9</sup> E. Wickers, *J. Am. Chem. Soc.* **76**, 2033 (1954).

<sup>1</sup> M. E. Fine, E. S. Greiner, and W. C. Ellis, *J. Metals* **191**, 56 (1951).

<sup>2</sup> H. Pursey, *Nature* **169**, 150 (1952); also *J. Inst. Metals* **8**, 362 (1958).

<sup>3</sup> M. E. Straumanis and C. C. Weng, *Acta. Cryst.* **8**, 367 (1955)

<sup>4</sup> G. K. White, *Australian J. Physics* **14**, 359 (1961).

<sup>5</sup> J. F. Marin, Technical Report No. 1, AEC Contract No. AT(04-3)221, California Institute of Technology, 1962 (unpublished). This report contains a reasonably complete bibliography of papers on Cr.

<sup>6</sup> D. I. Bolef, J. de Klerk, and R. W. Guernsey, *Bull. Am. Phys. Soc.* **6**, 76 (1961).

<sup>7</sup> G. Shirane and W. J. Takei, Proceedings of the International Conference on Magnetism, Kyoto, 1961 (to be published, 1962).

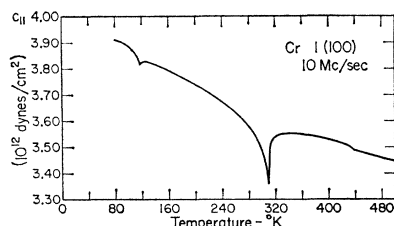


FIG. 1.  $c_{11}$  as a function of temperature. 10-Mc/sec longitudinal sound wave propagated along [100] axis of Cr No. 1.

as determined by x-ray diffraction. The lattice constant at  $T=298^\circ\text{K}$  was taken<sup>3</sup> to be  $\alpha_0=2.87918 \text{ \AA}$ . The value of Avogadro's constant used in the calculation of densities was  $N_0=6.0237 \times 10^{23}$ .

A high-frequency cw ultrasonic resonance technique was used to measure the acoustic velocities from which the elastic constants were computed. This technique has been described in some detail in previous papers, both as used at a fixed temperature<sup>10</sup> and over the temperature range 77 to  $500^\circ\text{K}$ .<sup>11</sup> The resonant response of the composite resonator, consisting of quartz transducer, bond, and specimen, is measured on a  $Q$  meter. The  $Q$ -meter frequency is monitored by a frequency counter. The velocity of sound in the specimen is related to the measured mechanical resonance frequencies by

$$v_{S,n} = (2l_S/n)[v_{C,n} + (m_T/m_S)(v_{C,n} - v_T)], \quad (1)$$

where  $m = \rho l$ ;  $\rho$  is the density;  $l$  is the length; and the subscripts  $S$  and  $T$  designate, respectively, the specimen and transducer.  $v_{C,n}$  is the observed mechanical resonance frequency corresponding to  $n$ , the effective number of half wavelengths of sound in the composite resonator:

$$n = (v_{C,n}/\Delta v_C)(1 - m_T/m_S), \quad (2)$$

where  $\Delta v_C$  is the measured frequency difference between adjacent half-wave resonance  $v_{C,n}$  and  $v_{C,n-1}$ . In Eqs. (1) and (2) the effect of the bond has been neglected.

The compressional elastic constant  $c_{11}$  and the shear constant  $c_{44}$  were obtained, respectively, from the measured velocities of sound of longitudinal and transverse waves propagated along the [100] crystal axis of Cr No. 1. The shear constants  $c_{44}$  and  $C' = \frac{1}{2}(c_{11} - c_{12})$  were obtained from the measured velocities of sound for transverse waves propagated along the [110] axis of Cr No. 2. The high attenuation of the longitudinal wave in Cr No. 2 precluded accurate measurements of  $C' = \frac{1}{2}(c_{11} - c_{12} + 2c_{44})$ . 10-Mc/sec transducers of diameter comparable to that of the specimens were used. Bonds of Nonaq stopcock grease and of GC8101 silicone grease were used.<sup>11</sup> The precision of the measured velocities was  $\pm 0.2\%$  or better.

<sup>10</sup> D. I. Bolef and M. Menes, J. Appl. Phys. 31, 1010 (1960).

<sup>11</sup> D. I. Bolef and J. de Klerk, J. Appl. Phys. 33, 2311 (1962).

TABLE II. Elastic properties of chromium.  $10^{12}$  dyn/cm<sup>2</sup>.

	$c_{11}$	$c_{44}$ [100]	$\frac{1}{2}(c_{11} - c_{12})$	$B = \frac{1}{3}(c_{11} + 2c_{12})$	$A = 2c_{44}/(c_{11} - c_{12})$	$\rho$ g/cc
77°K	3.91	1.032	1.507	1.91	0.68	7.223
298°K	3.50	1.008	1.411	1.62	0.71	7.200
500°K	3.46	0.987	1.349	1.66	0.73	7.163

Thermal expansion measurements were made between 77 and  $360^\circ\text{K}$  using a quartz dilatometer<sup>12</sup> which incorporated a linear variable differential transformer. The resolution of the dilatometer for small samples was  $10^{-5}$  in. or better.

### III. RESULTS

The experimental results of the elastic constant measurements at 77, 298, and  $500^\circ\text{K}$  are summarized in Table II. The elastic constants  $c$  were calculated from the measured velocities ( $c = \rho v^2$ ) using the values of density given in the last column. The density values as a function of temperature were obtained using the thermal expansion data of Fine *et al.*<sup>1</sup> and of Erfing<sup>13</sup> for polycrystalline chromium. These values of density differ at most by 0.1% (at  $77^\circ\text{K}$ ) from the single crystal [100] thermal expansion data reported in this paper. The values of the shear constant  $c_{44}$  are those obtained by measurements on Cr No. 1 [100].  $B$  is the adiabatic bulk modulus. The value of  $B$  at  $298^\circ\text{K}$  may be compared with the room-temperature value of the isothermal bulk modulus  $B_{is} = 1.6 \times 10^{12}$  dyn/cm<sup>2</sup> obtained by Bridgman.<sup>14</sup> In column six the values of the shear anisotropy ratios  $A$  are given. The values of elastic constants at  $298^\circ\text{K}$  are in good agreement with independent results obtained by Smith and Sumer.<sup>15</sup>

In Figs. 1 and 2 are shown the temperature dependences of the elastic constants of chromium. The anomaly

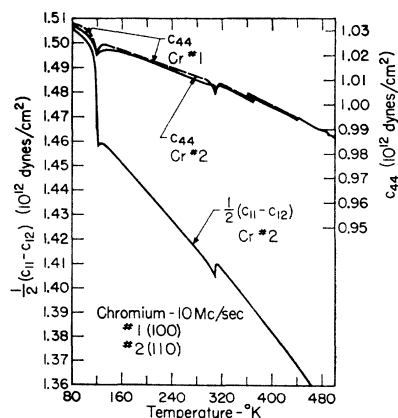


FIG. 2. Shear constants of chromium as a function of temperature.

<sup>12</sup> G. B. Brandt, Westinghouse Research Laboratories Report 62-108-108-R1, 1962 (unpublished).

<sup>13</sup> H. D. Erfing, Ann. Physik 34, 139 (1939).

<sup>14</sup> P. W. Bridgman, Proc. Amer. Acad. Arts Sci. 68, 27 (1932).

<sup>15</sup> J. F. Smith and A. Sumer (unpublished). We are indebted to Dr. Smith for communicating these results.

in  $c_{11}$  (Fig. 1) at 310°K is about 7%; at 120°K about 1.3%. In almost every respect, the curve of Fig. 1 shows a marked similarity to that of Fine *et al.*<sup>1</sup> for Young's modulus in polycrystalline chromium. The anomalies for  $c_{44}$  (Fig. 2) for sound propagated in the [100] and [110] directions are similar (if anything, more marked in the case of [110]). The apparent "break" in  $c_{44}$  at approximately 360°K was due to bonding difficulties. For all three shear modes, the low-temperature anomaly is more marked than that at 310°K. This is in sharp contrast to the behavior of  $c_{11}$ . The slight anomaly in  $c_{11}$  and  $c_{44}$  at approximately 440°K was reproducible.

Measurements of  $c_{11}$ ,  $c_{44}$ , and  $\frac{1}{2}(c_{11}-c_{12})$  were repeated over the temperature ranges including the high-temperature and low-temperature anomalies while the specimen was located in a magnetic field of 10 000 G. The measurements were made for  $H$  parallel to the [100] and [110] axes of the crystal. No differences in the behavior of the elastic constants were observed between the zero-field and maximum-field observations.

In order to show details of the elastic constant anomalies, the measured mechanical resonance frequencies (see Sec. II) as a function of temperature are plotted in Figs. 3 and 4. In Fig. 3 only the very tip of the  $c_{11}$  anomaly at 310°K is shown, for comparison with the shear anomalies. The structure in  $\nu_{c_{44}}$  (Cr No. 2) appeared to be real, as did the almost vanishingly small anomaly of  $\nu_{c_{44}}$  (Cr No. 1). Figures 3 and 4 are meant to show the shapes of the curves; since the sound velocity is related to the measured frequencies by the length of the specimen as well as by the number  $n$  of half wavelengths of sound in the specimen, no direct comparison of velocities can be obtained from only these detailed curves. In Fig. 5 is plotted the calculated curve of the volume compressibility  $\chi = 3/(c_{11} + 2c_{12})$  as a function of temperature. The values of  $\chi$  were obtained from those of  $c_{11}$  and  $C' = \frac{1}{2}(c_{11} - c_{12})$ ; e.g.,  $\chi = 3/(3c_{11} - 4C')$ . The anomaly at 440°K shows up strongly in the plot of volume compressibility.

FIG. 3. Details of the high-temperature anomaly at 310°K. Measured mechanical resonance frequency is plotted vs temperature.

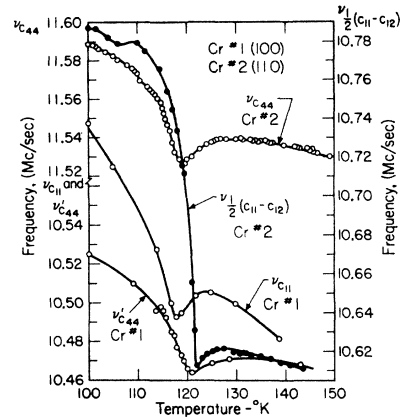
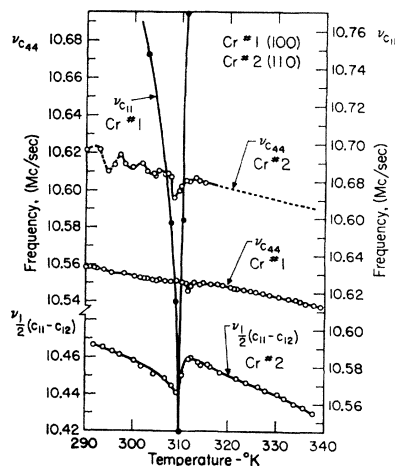


FIG. 4. Details of the low-temperature anomaly at 120°K. Measured mechanical resonance frequency is plotted vs temperature.

The thermal expansion results are shown in Figs. 6 and 7. Within the reproducibility of the data, the thermal expansivity curves ( $\Delta l/l_0$ ) were the same for Cr No. 1 [100] and Cr No. 2 [110]. In many of the runs, however, the thermal expansion anomaly for Cr [110] was less marked than that for Cr [100]. From Fig. 7 it can be seen that the coefficient of thermal expansion varies from  $7.5 \times 10^{-6}$  per deg C at 280°K through a minimum of  $1.5 \times 10^{-6}$  per deg C approximately at 310°K to  $9.5 \times 10^{-6}$  per deg C at 360°K.

#### IV. DISCUSSION

##### Antiferromagnetism in Chromium

That the anomaly in chromium at 310°K corresponds to a transition from a paramagnetic to an antiferromagnetic state has been demonstrated by neutron diffraction studies<sup>7,16</sup> and also by measurements of magnetic susceptibility. A lambda type anomaly at 312°K in the heat capacity of pure ductile chromium has also been reported.<sup>17</sup> The magnetic susceptibility measurements,<sup>18</sup> made on polycrystalline samples of various particle size and purity, showed an anomalous peak in the susceptibility at 313°K.

Recent neutron diffraction work on pure crystalline chromium and on single crystalline chromium has demonstrated most clearly the magnetic nature of chromium. The two most detailed reports are those of Bacon<sup>16</sup> and of Shirane and Takei.<sup>7</sup> Bacon's results on a single crystal of chromium, containing less than 0.003% oxygen by weight, revealed a Néel temperature at 313°K and a low-temperature transition at about 154°K. The latter transition was not observed in the polycrystalline chromium specimens investigated by Bacon. He reported that the magnetic moment on the chromium atom, below the Néel temperature, was

<sup>16</sup> G. E. Bacon, *Acta Cryst.* **14**, 823 (1961).

<sup>17</sup> R. H. Beaumont, H. Chikara, and J. A. Morrison, *Phil. Mag.* **5**, 188 (1960).

<sup>18</sup> E. W. Collings, F. T. Hedgcock, and A. Siddiqui, *Phil. Mag.* **6**, 155 (1961).

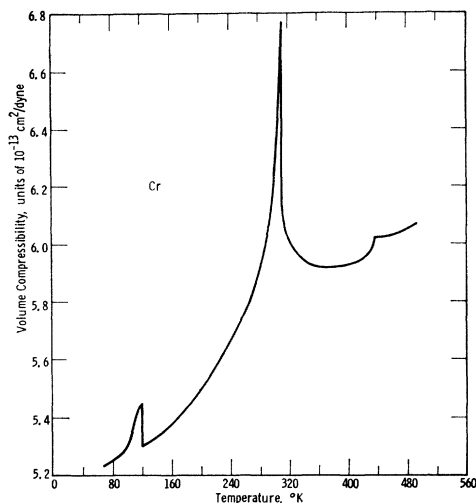


FIG. 5. Volume compressibility,  $\chi = 3(c_{11} + 2c_{12})^{-1}$  as a function of temperature.

about 0.45 Bohr magneton. The neutron diffraction experiments of Shirane and Takei were performed on the same single crystal, Cr No. 1, as was used in the present work, as well as on several iodide chromium single crystals. They report transitions at 310 and at 121°K, in agreement with the elastic constant anomalies reported in Sec. III. The low-temperature anomaly, attributed to a transition between two states of different antiferromagnetic ordering, has been observed only in elastic constant<sup>1,5</sup> and in neutron diffraction<sup>7,18,19</sup> work. The anomaly is reported to occur at 153°K by Bykov *et al.* and by Bacon. The other investigations, including the present work, report the anomaly at approximately 121°K.

Several interpretations of the magnetic scattering patterns in neutron diffraction have been offered. These include an antiphase antiferromagnetic domain structure<sup>20</sup> or a model of continuously spiralling spins,<sup>21</sup> both with periodicities of about 25 unit cells; and a model of a sinusoidal modulation of the magnetic scattering amplitude, with the spin direction parallel to the propagation vector below the 121°K transition and perpendicular to it above the 121°K transition.<sup>7</sup> The different possible models of antiferromagnetism in chromium have been discussed by Overhauser and Arrott.<sup>22</sup>

### Thermal Expansion Anomaly

The thermal expansivity curve (Fig. 6) shows a noticeable inflection, corresponding to a minimum in the

coefficient of thermal expansion, in the region of 310°K. The change in thermal expansion coefficient (Fig. 7) is  $\Delta\alpha \approx -7 \times 10^{-6}$  per deg C; this negative change in  $\alpha$  is in sharp contrast to the anomalous changes in thermal expansions at the Néel temperature of compound antiferromagnets such as MnO ( $\Delta\alpha \approx +50 \times 10^{-6}$  per deg C) and CoO ( $\Delta\alpha \approx +20 \times 10^{-6}$  per deg C),<sup>23</sup> and also in MnF ( $\Delta\alpha \approx +50 \times 10^{-6}$  per deg C).<sup>24</sup> Two tentative explanations have been proposed by White<sup>4</sup> for the thermal expansion anomaly in Cr. The first depends upon the existence of a large negative value for the electronic contribution,  $\alpha_e$ , to the thermal expansion, which might change appreciably due to the change in magnetic ordering at the Néel temperature. A detailed discussion of the electronic contribution to the thermal expansion has been given by Varley.<sup>25</sup> The second explanation is based on the concept of interactions between *d* shells, repulsive or attractive, depending upon whether the spins are parallel or antiparallel.<sup>26,27</sup> On the basis of this interaction, an increase in  $\Delta\alpha$  at the antiferromagnetic ordering temperature, such as is observed for the antiferromagnetic oxides, rather than a decrease, as in the present case, would be expected.

Based on considerations of the molecular field model of antiferromagnetism,<sup>28</sup> one expects that the magnetic energy will make a contribution to the coefficient of expansion, since the exchange integral *J* may vary with temperature. Lidiard<sup>28</sup> gives for the additional term in the coefficient of expansion, due to magnetic contribution to an isotropically expanding crystal,

$$\Delta\alpha = 2\chi Nz\bar{S}(d\bar{S}/dT)(d|J|/dv),$$

where  $\chi$  is the compressibility, *N* is the total number of magnetic ions, *z* is the coordination number,  $\bar{S}$  is the mean value of the spin for nearest neighbor atoms, and

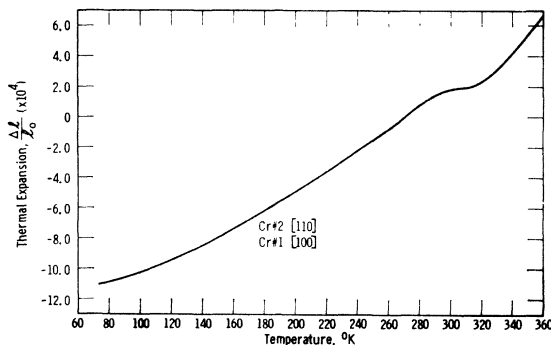


FIG. 6. Thermal expansivity is in units of  $10^{-4}$ . The specimen length at 0°K is  $l_0$ .

<sup>19</sup> V. N. Bykov, V. S. Golovkin, N. V. Ageev, V. A. Levdkin, and S. I. Vonogradov, *Doklady Akad. Nauk S. S. S. R.* **128**, 1153 (1959).

<sup>20</sup> L. M. Corliss, J. M. Hastings, and R. J. Weiss, *Phys. Rev. Letters* **3**, 211 (1959).

<sup>21</sup> T. A. Kaplan, *Phys. Rev.* **116**, 888 (1959).

<sup>22</sup> A. W. Overhauser and A. Arrott, *Phys. Rev. Letters* **4**, 226 (1960).

<sup>23</sup> M. Foex, *Compt. Rend.* **227**, 193 (1943).

<sup>24</sup> D. F. Gibbons, *Phys. Rev.* **115**, 1194 (1959).

<sup>25</sup> J. H. O. Varley, *Proc. Roy. Soc. (London)* **A237**, 413 (1956).

<sup>26</sup> C. Zener, *Trans. A.I.M.E.* **203**, 619 (1955).

<sup>27</sup> B. S. Chandrasekhar, *Acta. Met.* **6**, 212 (1958).

<sup>28</sup> A. B. Lidiard, in *Reports on Progress in Physics* (The Physical Society, London, 1954), Vol. 17, p. 201.

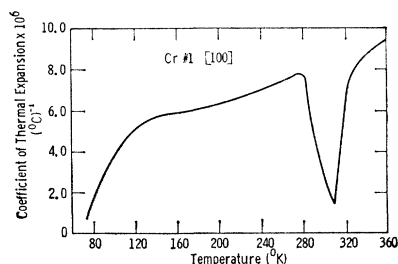


FIG. 7. Coefficient of thermal expansion,  $\alpha = (1/l)(dl/dT)$ , in units of  $10^{-6}$  per deg C.

$d|J|/dv$  is the derivative of the exchange integral with respect to the atomic volume. This expression can be rewritten in terms of the magnetic specific heat  $C_v$ ,

$$\Delta\alpha = -(\chi C_v/|J|)(d|J|/dv).$$

A sharp change in the compressibility should, therefore, be accompanied by a change in the coefficient of thermal expansion. The direction of change in the latter quantity will depend also on the sign of  $d|J|/dv$ .

Lacking a detailed microscopic explanation of the thermal expansion anomaly in antiferromagnetic chromium, one has recourse to purely thermodynamic theories of phase transitions of the second kind. At a lambda point transition, for example, the thermal expansion is related to the heat capacity  $C_P$  and compressibility  $\chi$  by the expression<sup>29</sup>

$$\Delta C_P = T_\lambda(\Delta\alpha)^2/\rho\Delta\chi,$$

where  $\Delta C_P$ ,  $\Delta\alpha$ , and  $\Delta\chi$  are the differences, at the transition temperature  $T_\lambda$ , between the observed and "normal" values of the physical variables.  $\rho$  is the density at the transition temperature. Using  $C_P = 0.15$  cal/g atom deg (see footnote 16),  $\Delta\chi \approx 1.02 \times 10^{-13}$  cm<sup>2</sup>/dyn,  $T_\lambda = 310^\circ\text{K}$ , and  $\rho = 7.20$  g/cm<sup>3</sup>, one obtains  $|\Delta\alpha| \approx 17 \times 10^{-6}$  per deg C. Considering that the specific heat measurements were made on a different chromium specimen, and allowing for experimental error in measuring the change in physical variable at the transition, this calculated value agrees reasonably well with the measured value of  $\Delta\alpha = -7 \times 10^{-6}$  per deg C.

### Elastic Constant Anomalies

The data in the present work were taken on two single crystals of similar impurity content. One cannot eliminate the possibility that anomalous effects (e.g.,

the slight difference in temperature dependence of  $c_{44}[100]$  and  $c_{44}[110]$ ) may be attributed to slight differences in impurity content. The presence of nitrogen, in particular, has been reported by many observers to be related to the intensity of the anomaly and to the temperature at which it occurs. This has been most recently investigated by James, Straumanis, and Rao,<sup>30</sup> who used x-ray techniques to measure the lattice constant in the region of the anomaly at the Néel temperature. Their results show that for increasing nitrogen content the temperature at which the anomaly occurs increases; and also that this temperature differs for two polycrystalline chromium specimens of same nitrogen content but different crystalline composition.

Perhaps the most striking aspects of the elastic constant results are (a) the relative magnitudes of the shear vs compressional anomalies at the high- and low-temperature transitions, and (b) the difference in the shapes of the two shear anomalies at the low-temperature transition. The latter comparison indicates that the change in spin configuration at the 120°K transition affects next-nearest neighbor interactions more than it does nearest-neighbor interactions. The high temperature anomaly at 440°K may be due to the presence of residual short-range order.

The reproducibility of the temperature dependence of the thermal expansion and elastic constants under conditions of varying cooling (and heating) rates through the transition temperatures indicates that the Cr crystals contained a multitude of domains whose "axes" were degenerate with respect to the cube axes of the crystal. Because of the antiferromagnetic ordering, one might expect that the elastic constants below the Néel temperature would be those characteristic of a hexagonal lattice; that this is not observed is also, probably, indicative of a multiple domain configuration. In such a situation, the observed "cubic" elastic constants must be considered as average values of the elastic constants appropriate to the "true" hexagonal lattice.

### ACKNOWLEDGMENTS

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<sup>29</sup> See, e.g., I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longmans Green and Company, London, 1954).

<sup>30</sup> W. J. James, M. E. Straumanis, and P. B. Rao, *J. Inst. Metals* **90**, 176 (1961).