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The Discontinuity of the X-ray Debye Temperature of Chromium near the Néel Temperature

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The integrated intensity of the lines 550 and 712 from a chromium powder sample was measured at 310·2 and 313·2°K, that is below and above the Neél temperature. From the difference in the integrated intensity of each line and after correction for thermal diffuse scattering, it was found that in this interval there exists a discontinuity in the Debye temperature of approx. 8°K. This discontinuity is 2·8 times larger than the one calculated from the discontinuity of the elastic constants data.

Introduction

Chromium shows anomalies in many of its properties at a temperature just above room temperature. Specifically, in the specific heat (Beaumont, Chihara & Morrison, 1960) and in the various elastic constants (Bolef & de Klerk, 1963; Straumanis & Weng, 1955; Robertson & Lipsitt, 1965). Wilson, Skelton & Katz (1966) measured the X-ray Debye temperature of chromium in the temperature interval 100 to 550°K; however, the accuracy was insufficient to establish the existence of a discontinuity of 3°K, as expected by calculation from elastic constant data.

Chromium is antiferromagnetic and its Néel temperature lies in the temperature region of the above anomalies so that they have been ascribed to the antiferromagnetic transition. The accurate determination of the Néel temperature of chromium has been the subject of many investigations, but the results do not agree with each other nor with the temperature of the anomalies mentioned above. Thus the question arose whether the disagreement might be due to impurities of the samples or to other causes. Although Corliss & Hastings (1959) found the Néel temperature at 308 ± 2°K, Bacon (1961, 1962) examining the discrepancies, concluded that the Néel temperature lies just below 313°K, that it is independent of impurity content in the sample, but may depend on the strains in the material due to various methods of preparation. Sabine & Cox (1966) on the contrary, found that plastic deformations have no effect on the Néel temperature.

In the present work comparison of the Debye temperature was undertaken at 310·2 and 313·2°K, *i.e.* at two temperatures between which the accepted value of the Néel temperature and the discontinuity in the specific heat lie (Beaumont, Chihara & Morrison, 1960).

Experimental details

The intensities of the 550 and 712 X-ray diffraction lines were measured at 310·2 and 313·2°K. The sample *S* (Fig. 1) was a thin rod made of 400 mesh chromium powder obtained from British Drug House Laboratory Chemical Group Ltd, and was fixed with Apiezon by one end on the ceiling of a small brass chamber *Ch*. The chamber was thermally insulated from the environment and had Mylar windows for the incident and diffracted beams. The chamber was fixed on the head of a two-circle goniostat which in turn was fixed upside down above a Unicam goniometer by support *Sp*. The sample was aligned with the goniometer axes. A Geiger counter eqiupped with a cylindrical collimator could be rotated in the equatorial plane. The ceiling of the chamber was welded to the end of a copper plate; at the other end the plate was welded to a large copper cylinder immersed in water in a Dewar flask. The water could be maintained at a constant temperature by a coil tube forming part of the closed water circuit of a thermostat. In this way the temperature of the interior of the chamber, as measured with the thermometer *Th*, could be kept constant within better than 0·1°K.

The sample was irradiated with Mo $K\alpha$; radiation with a longer wavelength would give only low index lines. The strong fluorescence of the sample was highly reduced by using aluminum foils of a total thickness of 160 μ put in front of the counter. The profile of line (550) was scanned point by point at 310·2°K and then at 313·2°K. Each point was measured until 1600 counts were registered. Due to the overlapping of the tails of neighbouring lines, an accurate background could not be determined, hence the area between the curve and a straight line joining the minima on either side of the curve was considered to be a measure of the integrated intensity. By planimetering the profile, the change of the integrated intensity between the two temperatures was determined. This procedure was repeated 20 times thus giving 20 independent values of the change of the intensity. The experiment was then repeated with line (712) to the same accuracy as above. Two such independent runs were performed. In Fig. 2 the average form of such a profile is plotted, using the mean values of the counting rate for each point. The indicated statistical error thus corresponds to 32000 counts per point. The two peaks correspond to $K\alpha_1$ and $K\alpha_2$; the angle $\varphi = 180° - 2\theta$ is the reading on the circle *Gc* of the goniometer.

Calculations and results

The integrated intensity of a diffraction line is given by (James, 1958)

$$J = C \exp\{-2M[T, \Theta(T)]\} \tag{1}$$

where C is a factor which in this experiment can be considered as constant for each line.

In the Debye–Waller factor with the usual notation

$$2M = \frac{12h^2}{m_\alpha k}\left(\frac{\sin\theta}{\lambda}\right)^2 \cdot \left[\Phi(\chi) + \frac{\chi}{4}\right]\frac{T}{\Theta^2} \tag{2}$$

we have

$$\Phi(\chi) = \frac{1}{\chi}\int_0^{\chi}\frac{\xi \mathrm{d}\xi}{e^\xi - 1} \qquad \chi = \frac{\Theta}{T}, \qquad \xi = \frac{h\nu}{kT}.$$

The values of the integral are found from *International Tables for X-ray Crystallography* (1959) giving the function $\Phi(\chi)$ against χ. Considering Θ as a function of temperature and differentiating (1) we obtain

$$\begin{aligned}\frac{\mathrm{d}J}{J} &= \frac{12h^2}{m_\alpha k}\cdot\left(\frac{\sin\theta}{\lambda}\right)^2 \\ &\times\left\{\left[\frac{1}{T(e^{\Theta/T}-1)} - \frac{2T}{\Theta^2}\int_0^{\Theta/T}\frac{\xi\mathrm{d}\xi}{e^\xi-1}\right]\frac{\mathrm{d}T}{\Theta}\right. \\ &\left.+\left[\tfrac{1}{4} - \frac{1}{e^{\Theta/T}-1} + \frac{3T^2}{\Theta^2}\cdot\int_0^{\Theta/T}\frac{\xi\mathrm{d}\xi}{e^\xi-1}\right]\frac{\mathrm{d}\Theta}{\Theta^2}\right\}.\end{aligned} \tag{3}$$

This formula relates the change dJ with dT and dΘ.

Because the thermal diffuse scattering (TDS) is contained in the measured integrated intensity, we write

$$J_{\text{meas}} = J + J_{\text{TDS}}$$

and corrected the results (Chipman & Paskin, 1959) according to the formula:

$$J_{\text{meas}} = C\exp\{-2M(1-\beta)\}$$

where

$$\beta = 2\pi a^3 g^2_{\max}\cdot\frac{\cos\theta}{3n\lambda}\cdot\Delta\theta$$

In the last formula a is the lattice constant, n the number of atoms per unit cell, $\frac{4}{3}\pi g^3_{\max}$ is the volume of the first Brillouin zone and $\Delta\theta$ the angular length of the background line.

For a body-centred cubic lattice

$$\beta = \sqrt[3]{\frac{\pi}{12}}\cdot\frac{a\cos\theta}{\lambda}\cdot\Delta\theta$$

Finally (3) becomes:

$$\begin{aligned}\frac{\mathrm{d}J_{\text{meas}}}{J_{\text{meas}}} &= \frac{12h^2}{m_\alpha k}\cdot\left(\frac{\sin\theta}{\lambda}\right)^2\cdot\left[1 - \sqrt[3]{\frac{\pi}{12}}\cdot\frac{a\cos\theta}{\lambda}\cdot\Delta\theta\right] \\ &\times\left\{\left[\frac{1}{T(e^{\Theta/T}-1)} - \frac{2T}{\Theta^2}\int_0^{\Theta/T}\frac{\xi\mathrm{d}\xi}{e^\xi-1}\right]\cdot\frac{\mathrm{d}T}{\Theta}\right. \\ &\left.+\left[\tfrac{1}{4} - \frac{1}{e^{\Theta/T}-1} + \frac{3T^2}{\Theta^2}\cdot\int_0^{\Theta/T}\frac{\xi\mathrm{d}\xi}{e^\xi-1}\right]\cdot\frac{\mathrm{d}\Theta}{\Theta^2}\right\}\end{aligned}$$

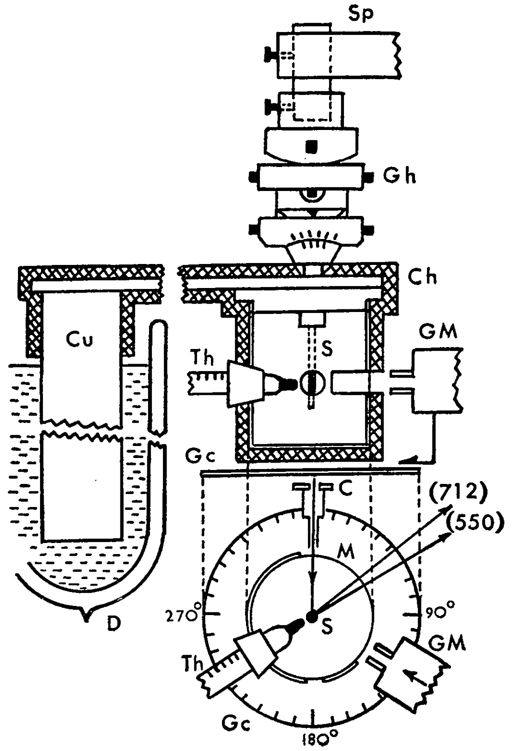

Fig. 1. The experimental instrument. *Sp* support fixing a two-circle goniostat above a Unicam goniometer, *Gh* goniostat, *Ch* brass chamber, *GM* Geiger–Müller tube, *Th* thermometer, *Gc* goniometer circle, *C* source of Mo $K\alpha$ radiation, *M* Mylar windows, *S* sample, Cu copper cylinder, *D* Dewar flask.

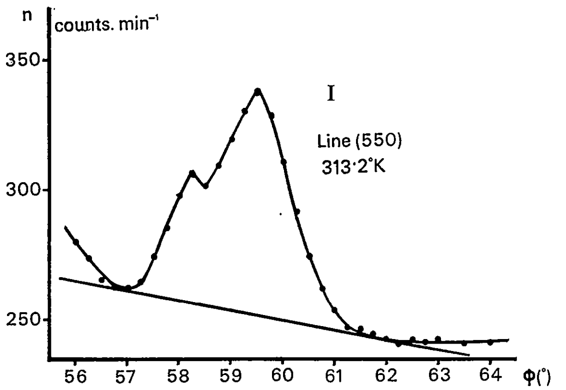

Fig. 2. The 550 line at 313·2°K. The vertical line indicates the maximum statistical error.

For the ratio $dJ_{\text{meas}}/J_{\text{meas}}$ we insert the planimetering values. The characteristic temperature ($\Theta = 543\,^\circ$K) of chromium at 310°K was obtained from the work of Wilson *et al.* (1966).

The following results were obtained from the calculations:

$$\Delta\Theta_{(550)} = 8{\cdot}0 \pm 1{\cdot}0\,^\circ\text{K}$$
$$\Delta\Theta_{(712)A} = 7{\cdot}3 \pm 0{\cdot}8\,^\circ\text{K}$$
$$\Delta\Theta_{(712)B} = 8{\cdot}2 \pm 0{\cdot}6\,^\circ\text{K}$$

The statistical error quoted was determined from the variation of the experimental values of

$$\frac{dJ_{\text{meas}}}{J_{\text{meas}}} .$$

These results are summarized as

$$\Delta\Theta = 7{\cdot}9 \pm 0{\cdot}8\,^\circ\text{K}$$

This result is about 2·8 times larger than the one calculated from the discontinuity of the elastic constants (Wilson *et al.*, 1966).

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Electron Population Analysis of Accurate Diffraction Data. I. Formalisms and Restrictions

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A two-dimensional polynomial method is described which allows rapid evaluation of bond-scattering factors in a structure factor least-squares program. Correlation effects between electron population parameters are analyzed. It is concluded that simultaneous refinement of $2s^2$ and three $2p^2$ one-center populations is not possible. Similarly, for the y axis being along a bond AB, the distributions $p_x(A)p_z(B)$ and $p_z(A)p_x(B)$ are identical and only the sum of the corresponding population parameters can be refined. A variety of models is discussed, in which the number of parameters is reduced by selective elimination. In the *two-center model* all terms but those describing 'long' bonds are included. In the *symmetry-restricted two-center model* all bonds are required to have *mm* symmetry, while in the *one-center model* all two-center terms are neglected. Finally, a full table of symmetry restrictions on population parameters and a brief discussion of thermal motion treatment are given.

Introduction

With the improvement in experimental accuracy made possible by diffractometers the information contained in diffraction data has increased considerably.

One of the potentially important extensions of X-ray crystallography is the study of electron distribution in crystals. For molecular crystals the interest is focused on the redistribution of the electron upon the formation of a molecule, or, in other words, upon the study of the covalent bond. In the last few years evidence has accumulated which shows that X-ray diffraction data can be used for such a purpose. In particular, it has been realized that the amazing, and continuing, success of the spherical atom model is due to a refinement of electron density features through adjustment of anisotropic temperature parameters and atomic positions. This can be illustrated through a combination of X-ray and neutron diffraction data (Coppens 1967; Coppens, Sabine, Delaplane & Ibers, 1969; Coppens & Vos, 1971) or by the use of high-order X-ray thermal parameters (Stewart & Jensen, 1969; Verschoor, 1967).