values are in general still larger than the standard deviations expected for accurate structure determinations at low temperatures [for an example, see Verschoor & Keulen, 1971; $\sigma(\mathrm{C})=0{\cdot}0007$ Å]. For the HO refinements, on the other hand, the systematic errors are smaller than the standard deviations obtainable for accurate experimental studies [for $B(H)$ only if f(SDS) is applied]. Our findings agree with the observation that differences between structural parameters obtained by X-ray and neutron diffraction decrease when a higher proportion of high-order X-ray reflexions is included in the X-ray refinement (Coppens & Vos, 1971).

It is easy to see that a change in the isotropic overall temperature factor from $\exp(-1{\cdot}07\sin^2\theta/\lambda^2)$ to $\exp(-B\sin^2\theta/\lambda^2)$ corresponds to a change in the least-squares weighting scheme from the adopted $w=1$ to $w=\exp[-2(B-1{\cdot}07)\sin^2\theta/\lambda^2]$. For increasing B values the weights of the high-order reflexions decrease, so that the shifts of an FA refinement will approach those of an LO refinement. For $B=2{\cdot}12$ Å^2 the FA refinement gives, for instance, $\Delta z(C)=-0{\cdot}0081$ Å.

Discussion

The study in the previous sections has shown that the reduction in height of the bonding maxima as observed for curve *b* in Fig. 3, is mainly due to errors in the atomic parameters rather than to series termination effects. To obtain reliable parameters HO refinements are necessary. This implies that accurately measured high-order reflexions as well as low-order reflexions must be available to obtain reliable difference densities by X-ray diffraction alone. The intensity measurements should therefore be done at low temperatures (preferably 'He temperatures') to reduce the thermal motion of the molecules as much as possible.

As an alternative, one can use neutron diffraction in addition to X-ray diffraction for the accurate determination of the parameters. If this has been achieved, a difference synthesis calculated with X-ray diffraction reflexions up to $H\simeq 1{\cdot}3$ Å^{-1} is expected to give a good picture of the bonding effects, except for regions close to the atomic nuclei.

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The Anomaly of the X-ray Debye Temperature of Chromium in the Temperature Range 35–51°C

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The integrated intensities of the 550 and 651 diffraction lines from a chromium single crystal were measured in the temperature range 35–51°C by steps of 2°C. A plot of the intensities of these lines *versus* temperature showed an abrupt change between 43 and 45°C corresponding to a discontinuity of about (3·6 ± 1·1)°C for the Debye characteristic temperature. This value is in good agreement with the one calculated from the discontinuity of the elastic constants.

Introduction

Chromium, which is antiferromagnetic, has kept the interest of many investigators because of its anomalous properties near the Néel temperature. They were concerned mainly with the specific heat (Beaumont, Chihara & Morrison, 1960), and the elastic constants (Bolef & De Klerk, 1963; Roberson & Lipsitt, 1965; Palmer & Lee, 1971). Similar anomalies were expected in the X-ray Debye temperature. Calculations from elastic constants lead to a discontinuity of 3°C (Wilson, Skelton & Katz, 1966). However, the existence of such

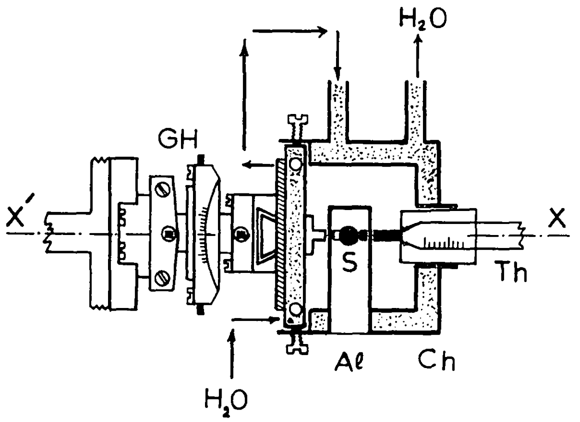

Fig. 1. The heating chamber with the goniometer head.

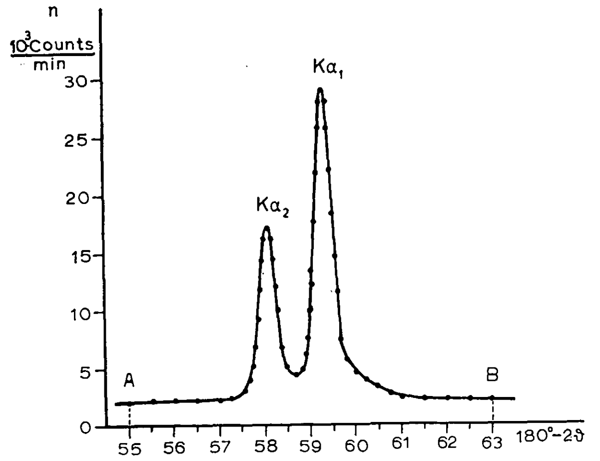

Fig. 2. The 550 line at 35 °C. The statistical error is too small to be shown.

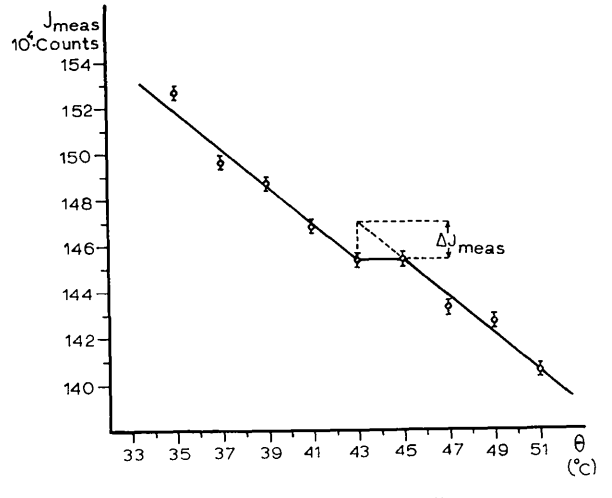

Fig. 3. The integrated intensity of the 550 line *versus* temperature

a small discontinuity could not be established from the measurements carried out by Wilson *et al.* in the temperature range 100–520 °K.

Koumelis (1971), working with X-rays on a 400 mesh powder sample, detected between 37 and 40 °C a discontinuity in the Debye temperature of about 7·9 ± 0·8C°. In the present experiment, the integrated intensities of the 550 and 651 diffraction lines from a single crystal were measured in the temperature range 35–51 °C by steps of 2 °C. The 550 and 651 lines and Mo *Kα* radiation were chosen because they give large $\sin \theta/\lambda$.

Experimental details

The sample used was a 4*N*5 purity chromium single crystal in the form of a cylinder with 8 mm diameter and 4mm height obtained from Metal Research Ltd,. Melbourne, England. The axis of the cylinder was [110]. Before use, the base was polished and etched. The sample *S* was fixed in a small double-walled chamber *Ch* (Fig. 1). Water from a thermostat circulated through the hollow walls and base. The temperature in the interior of the chamber measured by the thermometer *Th* could be kept constant within better than 0·1 °C. A 40μm aluminum window allowed the passage of the incident and diffracted beams. The chamber was fixed on a goniometric head *GH* and regulated so as to bring $[1\bar{1}\bar{1}]$ in coincidence with the goniometer axis *XX'*, and consequently the [550] and [651] directions on the meridian of the goniometer. An extension of this axis was fitted into a modified Philips diffractometer.

Fig. 2 shows the 550 line of chromium at 35 °C taken with Mo *Kα* radiation. The integrated intensity for each line and for each temperature was measured as follows: The line was scanned automatically from the position *A* to the position *B* ten times ($\theta, 2\theta$ scanning), and the total counts *N* and time *t* were registered. Afterwards, the counter was left for 10^3 s in the position *A* and the rate n_A of the counts was found; the same procedure was used for the position *B*. The integrated intensity *J* for the line was then:

$$J = N - \frac{n_A + n_B}{2} \cdot t .$$

Ten independent series of measurements were taken for each line and temperature.

Calculations and results

The integrated intensity of a diffraction line is given by:

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

(James, 1958), where *C* is a factor which in this experiment can be considered as constant for each line, and $2M$ is the Debye–Waller factor with the usual notation:

$$2M = \frac{12h^3}{m_a k}\left[\frac{\sin\theta}{\lambda}\right]^2\left[\varphi(x) + \frac{x}{4}\right] .$$

In this last equation we have:

$$x=\frac{\Theta}{T}\quad \xi=\frac{h\nu}{kT}\quad \varphi(x)=\frac{1}{x}\int_0^x \frac{\xi d\xi}{e^{\xi}-1}\,.$$

Differentiating (1) with respect to Θ we obtain:

$$\frac{dJ}{J}=\frac{12h^2}{m_\alpha k}\left[\frac{\sin\theta}{\lambda}\right]^2\left[\frac{1}{4}-\frac{1}{\exp(\Theta/T)-1}+\frac{3T^2}{\Theta^2}\cdot\int_0^{\theta/T}\frac{\xi d\xi}{e^{\xi}-1}\right]\frac{d\Theta}{\Theta^2}\,. \tag{2}$$

This formula relates the change dJ with $d\Theta$ for a given temperature T. As the thermal diffuse scattering (TDS) is contained in the measured integrated intensities, we write:

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

If we put:

$$J_{\text{TDS}}=\alpha J$$

we will have:

$$J_{\text{meas}}=J(1+\alpha)\,. \tag{3}$$

The factor α is equal to:

$$\alpha=\frac{8\pi kT}{3\lambda^3}\sin^3\theta\cos\theta\Delta\theta\mu \tag{4}$$

(Nilsson, 1957), where $\Delta\theta$ is the angular length of the background and μ is a function (Schwartz, 1964) of the elastic constants c_{ij}:

$$\mu=\frac{21(c_{11}+c_{12})(c_{11}-c_{12}-2c_{44})+105c_{44}(2c_{11}+c_{44})}{(c_{11}-c_{12}-2c_{44})[(c_{11}-c_{12}-2c_{44})(c_{11}+2c_{12}+c_{44})+21c_{44}(c_{11}+c_{12})]+105c_{11}c_{44}^2}\,.$$

The values of c_{11}, c_{12} and c_{44} were obtained from Palmer & Lee (1971).

Figs. 3 and 4 show the measured intensities of the 550 and 651 lines *versus* temperature. As the intensity is approximately a linear function of the temperature, we drew straight lines through the measured points. The lines were plotted by the least-squares method. It is evident that a discontinuity exists in the lines between 43 and 45 °C. From the least-squares method we obtain $dJ_{\text{meas}}/J_{\text{meas}}$ and using (2) we find before correction for TDS:

$$\Delta\Theta_{550}=4{\cdot}2\pm0{\cdot}8\,^{\circ}\text{C}$$

$$\Delta\Theta_{651}=2{\cdot}6\pm1{\cdot}4\,^{\circ}\text{C}\,.$$

Considering the values as equally probable, we write:

$$\Delta\Theta=3{\cdot}4\pm1{\cdot}1\,^{\circ}\text{C}\,.$$

Using (6) to correct for TDS we find:

$$\Delta\Theta=3{\cdot}6\pm1{\cdot}1\,^{\circ}\text{C}\,.$$

This value is in good agreement with the one calculated from the discontinuity of the elastic constants (Wilson *et al.*, 1966). The present value is smaller than the value found for the powder (Koumelis, 1971), and is considered more reliable, because the powdered sample was made by grinding granular polycrystalline material which probably causes plastic deformation.

Writing for (4):

$$\alpha=A\mu$$

and differentiating (3) we have:

$$\frac{dJ_{\text{meas}}}{J_{\text{meas}}}=\frac{Ad\mu}{1+A\mu}+\frac{dJ}{J}\,. \tag{5}$$

If we accept equality between the velocity of the longitudinal and transverse waves, the Debye frequency ν_D will be proportional to this common velocity, and hence ν_D^2 will be a linear function of the c_{ij}.

We then put approximately:

$$\Theta^2=Bc_{ij}$$

where B is a constant. Differentiating this last equation we have:

$$dc_{ij}=2c_{ij}\frac{d\Theta}{\Theta}$$

and

$$d\mu=-2\mu\frac{d\Theta}{\Theta}\,.$$

Substituting in (5) we find:

$$\frac{dJ_{\text{meas}}}{J_{\text{meas}}}=-\frac{2A\mu}{1+A\Theta}\frac{d\Theta}{\Theta}+\frac{dJ}{J}\,. \tag{6}$$

The position of the anomaly, *i.e.* between 43 and 45 °C, is in agreement with a previous experiment on the same crystal (Koumelis, 1973) according to which the Néel temperature was found at 43·3 °C.

The authors would like to thank Dr. S. Mourikis for helpful discussions.

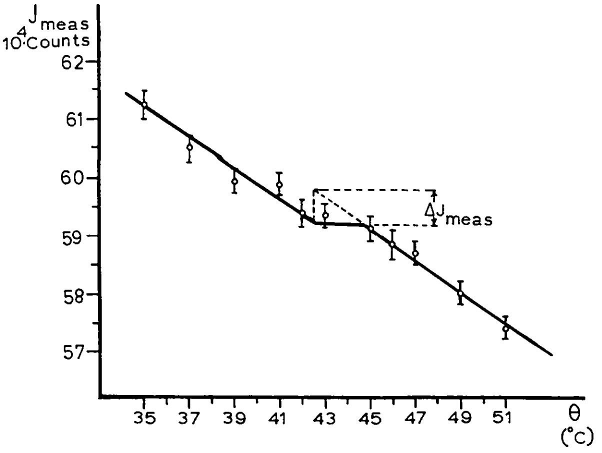

Fig. 4. The integrated intensity of the 561 line *versus* temperature

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X-ray Diffraction from Close-Packed Structures with Stacking Faults. I. *hcc* Crystals

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The kinematical theory of X-ray diffraction by *hcc* crystals with growth and deformation faults is developed. The intensity distribution in reciprocal space is derived as a function of five parameters which represent three growth and two deformation fault probabilities. Only reflexions with $H-K\neq 3N$, N an integer, are affected by faulting and generally exhibit changes in integrated intensity and broadening. In addition, reflexions with $L=6M\pm 1$ and $6M\pm 2$, M an integer, exhibit profile peak shift and profile asymmetry. It is shown that nine independent combinations of the five fault probabilities can be determined from the measured profile characteristics.

Introduction

X-ray diffraction from faulted close-packed crystals with a range of influence equal to 2, *i.e.*, *h* and *c* crystals [Jagodzinski (1949*a*) configurational symbols for h.c.p. and f.c.c. crystals respectively] has been considered by several authors. Wilson (1942) and Hendricks & Teller (1942) considered the case of growth faults while Patterson (1952) and Christian (1954) have considered deformation faults. (A growth fault arises when during the layer-by-layer growth of a crystal, the stacking rule is not obeyed in adding one new layer, but is otherwise obeyed throughout the crystal, while a deformation fault arises through the process of glide of one part of the crystal with respect to the remainder.) A general treatment for *h* and *c* crystals containing growth and deformation faults simultaneously has been given by Gevers (1954). Effects of extrinsic faults for *h* and *c* crystals have been found by Lele, Anantharaman & Johnson (1967) and Johnson (1963) respectively. (For *h* and *c* crystals, an extrinsic fault arises through the insertion of a close-packed layer.) Alternative treatments for extrinsic faults in *h* crystals and for deformation and extrinsic faults in *c* crystals have been given by Holloway (1969), Warren & Warekois (1955) and Warren (1963) respectively. The work has been reviewed by Warren (1959) and Wagner (1966).

X-ray diffraction from faulted close-packed crystals with a range of influence equal to 3, *i.e.*, *hc* (d.h.c.p.) crystals has been considered by Jagodzinski (1949*b*) for two types of growth faults and by Gevers (1954) and Lele, Prasad & Anantharaman (1969) for deformation faults. Prasad & Lele (1971) have given a comprehensive treatment for a total of nine types of fault (including the above three types).

There are three close-packed crystal structures with a range of influence equal to 4, namely *hcc*, *hhc* (samarium type) and *hhcc* structures. Gevers (1954) has given a general treatment for crystals of these three types containing growth faults as also for one type of deformation fault in *hcc* crystals. The object of the present paper is to complement the work on *hcc* crystals by carrying out the calculations to a stage where the fault probabilities are directly related to the experimentally observable diffraction effects. Further, unlike Gevers, we distinguish between deformation faults occurring between an *hh*, *hc* and *cc* pair of layers as they lead to configurations which are not equivalent energetically.

The *hcc* structure can be considered as a layer structure produced by the regular stacking of close-packed layers in the sequence $ABCACB,A$ where the letters A, B and C denote the three possible positions of the close-packed layers and the comma marks the completion of the repeat period (unit cell). The geometrical structure factors for different H,K,L are given in Table 1. A different notation (Nabarro, 1967) for the growth and deformation faults, virtual processes for their forma-