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Debye Characteristic Temperature as a Measure of the Ordering Parameter. II. Application to α-Brass

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The usual method of X-ray diffraction for determining the ordering parameter cannot be applied to α-brass. This problem has been solved by considering the Debye characteristic temperature, rather than the intensity of a diffraction line, as a measure of the parameter. By using the expression obtained in part I of this series of papers [Mitra & Chaudhuri (1974). *Acta Cryst.* A**30**, 385–387], the Debye characteristic temperatures of α-brass at different values of the ordering parameter have been calculated. From the X-ray diffraction data of α-brass after different heat treatments the Debye characteristic temperatures were determined. The ordering parameters were obtained by comparing the experimental values of the Debye characteristic temperatures with the theoretical values.

1. Introduction

It is well known that the usual X-ray method for determining the ordering parameter in alloys is not applicable to α-brass. This is because the atomic scattering factors of copper and zinc which are the constituents of the alloy, are so very similar that the diffuse X-ray scattering due to short-range order and the superlattice lines due to long-range order are too weak to be detected. In the case of β-brass Jones & Sykes (1937) used zinc radiation to detect the ordering. This, however, fails for α-brass. On the other hand, changes in many physical properties of α-brass as a result of various treatments (thermal, irradiation *etc.*), have been interpreted by authors, *e.g.*, Damask (1956), as changes in the degree of ordering. These changes may also be interpreted on the basis of other effects as well. Thus an unambiguous and quantitative detection and determination of the ordering parameter in α-brass, though it would have been extremely useful, was not developed until a method of determining the ordering parameter s from the knowledge of Debye characteristic temperature of the alloy was developed by the authors; details of it have been reported in paper I (Mitra & Chaudhuri, 1974). In the course of present investigation this theory has been successfully applied to α-brass.

2. Experimental

2.1 *Preparation of the samples*

The sample was prepared by induction melting with appropriate quantities of high-purity copper and zinc in a graphite crucible. Care was taken to mix the components adequately. To remove the segregation the sample was hot worked and was homogenized by heating at 450°C for 72 h. It was then slowly cooled. Finely powdered samples were made by filing, passed through sieve and then annealed at about 400°C for 6 h in a vacuum annealing furnace to remove the defects produced by cold working. Five samples were prepared by quenching from 27, 100, 200, 300 and 400°C. These powders were mixed with collodion and cakes were made on standard sample holders for an X-ray diffractometer. The surface of the sample was made extremely smooth by polishing.

2.2 *Study of the distribution of intensity*

The intensity distribution in the X-ray diffraction lines was determined to the use of a Norelco X-ray diffractometer with a Geiger counter and a decade counting system. Nickel-filtered copper radiation was used and the X-ray tube was operated with a highly-stabilized power supply at 35 kV and 10 mA. The angular setting was carried out manually and intervals of 0·01° near a peak and 0·05° at the background were used. The statistical fluctuation error was kept at less than 1% throughout the experiment by taking large counts. Three readings were taken at each setting and mean values taken.

2.3 *Corrections applied to the intensity data*

The intensity distribution was corrected for temperature diffuse scattering by the method of Chipman & Paskin (1959). The effect due to tails of the diffraction profiles was allowed for by a proper choice of the background level (Mitra & Misra, 1966). To avoid any preferred-orientation effects the experiment was repeated with several samples.

2.4 *Determination of the Debye characteristic temperature*

The integrated intensity $I_{\rm obs}$ of X-rays reflected by a set of crystallographic planes is given by James (1962)

$$I_{\rm obs}=kAmpf^2\exp\left(-2B\right)\frac{\sin^2\theta}{\lambda^2} \tag{1}$$

where k is the scale factor, A the absorption factor, m the multiplicity factor, p the Lorentz–polarization factor, f the atomic scattering factor, θ the Bragg angle corresponding to the reflecting planes and λ the wavelength of X-rays used.

The atomic scattering factors used were taken from Cromer & Waber (1965) who computed them from relativistic self-consistent field functions. The atomic scattering factors were corrected for anomalous dispersion.

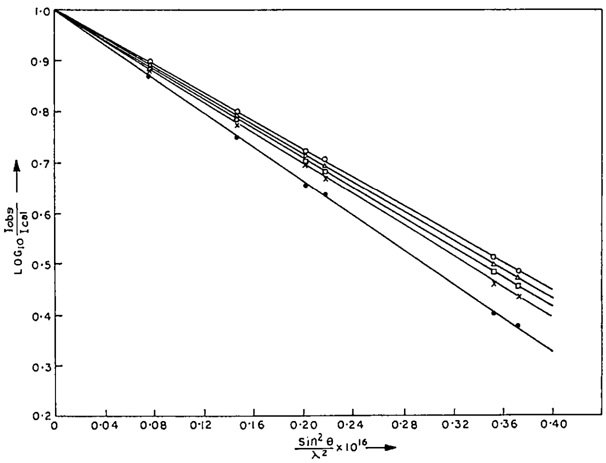

Fig. 1. Determination of the Debye temperature from the slope of the plot of log ($I_{\text{obs}}/I_{\text{cal}}$) against sin $^2\theta/\lambda^2$

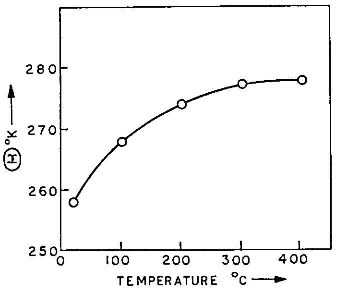

Fig. 2. Variation of Debye temperature with temperature.

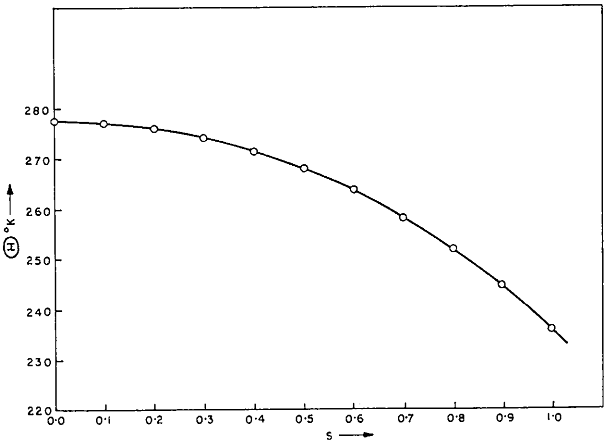

Fig. 3. Variation of Debye temperature with state of ordering.

The temperature factor B is given by

$$B=\frac{6h^2}{mKT}f(x) \tag{2}$$

where

$$f(x)=\left[\frac{\varphi(x)}{x^2}+\tfrac{1}{4}x\right]$$

$$x=\frac{\Theta}{T}$$

$$\varphi(x)=\frac{1}{x}\int_0^x \frac{\xi \mathrm{d}\xi}{e^{\xi}-1} \tag{3}$$

and h is Planck's constant, K Boltzmann's constant, m the mass of the vibrating atom, Θ the Debye characteristic temperature, and T room temperature.

Equation (1) can be written as

$$\ln\left(\frac{I_{\text{obs}}}{AmPf^2}\right)=\ln k-\frac{2B\sin^2\theta}{\lambda^2}\,. \tag{4}$$

From the slope of the linear plot of ln ($I_{\text{obs}}/AmPf^2$) against $\sin^2\theta/\lambda^2$ the value of B can be determined and thus the value of $f(x)$ can be found from equation (2). From the plot of $f(x)$ against x [*i.e.* from equation (3)], x can be determined corresponding to $f(x)$. Then from x, Θ can be found out from the relation $x=\Theta/T$.

2.5 *Determination of order parameter*

The final expression connecting the Debye characteristic temperature with the ordering parameter s is given by (paper I)

$$\begin{aligned}\Theta^2_{AB(pq)}M_{AB(pq)}=&\,p^2[\Theta^2_A M_A+\Theta^2_B M_B-2\Theta^2_{AB}M_{AB}]\\ &-2p[\Theta^2_B M_B-\Theta^2_{AB}M_{AB}]+\Theta^2_B M_B\\ &-p^2s^2[\Theta^2_A M_A+\Theta^2_B M_B-2\Theta^2_{AB}M_{AB}]\end{aligned} \tag{5}$$

where $\Theta_{AB(pq)}$, Θ_A and Θ_B are the Debye characteristic temperatures of the alloy $AB(pq)$ and the component metals A and B of atomic weights $M_{AB(pq)}=pM_A+qM_B$, M_A and M_B respectively, and Θ_{AB} is the Debye characteristic temperature of the fictitious lattice AB composed of atoms of atomic weight M_{AB}. The constant $\Theta^2_{AB}M_{AB}$ of the fictitious lattice has been calculated from the Debye characteristic temperature of the alloy for complete disorder state $s=0$. The variation of $\Theta_{AB(pq)}$ of the alloy with s as calculated from (5) will give the ordering parameter of the alloy subjected to different heat treatments.

3. Results and discussion

Fig. 1 shows the plot of log ($I_{\text{obs}}/I_{\text{cal}}$) against $\sin^2\theta/\lambda^2$ for several samples heat-treated at different temperatures. The values of Θ were calculated from the slopes by using the method described in § 2.4. It is shown in Fig. 2. It is observed that the Debye characteristic temperatures vary with the temperature of heat-treatment. Generally the Debye characteristic temperature changes as a function of the various types of defect concentration, such as particle size, strain, dislocation density *etc.* (Mitra & Chattopadhyay, 1972), but as these samples are well annealed, it is evident that they are free of all these defects. Thus this change of Debye characteristic temperature must be due to a change in local ordering. Fig. 3 shows the variation of Debye characteristic temperature with the ordering as calculated from equation (5). This graph was drawn after the constant $\Theta^2_{AB}M_{AB}$ had been calculated from the known value of $\Theta^2_{AB(pq)}M_{AB(pq)}$ at a heat-treatment temperature of 400°C when s can safely be taken to be zero, *i.e.* the alloy can be considered to be fully disordered. Thus, by determining the Debye characteristic temperatures of the samples quenched from different temperatures, the corresponding ordering parameter s can be found from the graph. The plot of ordering parameter s against temperature is shown in Fig. 4 from which it can be observed that the ordering decreases, as expected, with increase of temperature.

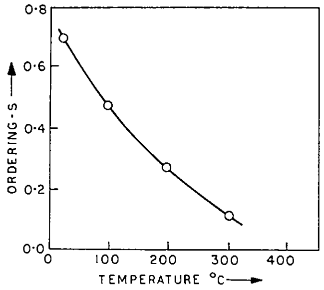

Fig. 4. Variation of ordering with temperature.

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A New Scheme for Seminvariant Tables in All Space Groups

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A new scheme is proposed to make the Hauptman–Karle Tables on structure seminvariants conform with international notation. An alternative derivation of the Tables for conventionally centred cells is presented.

The fundamental papers of Hauptman & Karle (1953, 1956, 1959; Karle & Hauptman, 1961) have excellently solved the problem of choosing an origin by specifying the values of an appropriate set of phases. Four tables, containing among other things the permissible origins and seminvariant moduli, have been presented in these papers; subsequently they were slightly modified (Karle, 1970).

Because of the considerable increase in the use of direct methods, these tables could be usefully issued in the new *International Tables for X-ray Crystallography*; nevertheless some modifications could be made for two reasons:

(*a*) to simplify their use, by a suitable notation similar to other crystallographic notations,

(*b*) to allow, in space groups with conventional centred cells also, the automatic search for permissible origins and seminvariant reflexions by the use of symmetry transformations (Hall, 1970; Gramaccioli & Zechmeister, 1972).

To pursue these two aims, some new definitions are necessary.

(1) *Permissible origins*: Hauptman & Karle (here H–K) define the permissible origins for primitive centrosymmetric space groups to be the eight points

$$\varepsilon_1,\varepsilon_2,\varepsilon_3;\ \varepsilon_i=0 \text{ or } \tfrac{1}{2},\quad i=1,2,3. \tag{1}$$

For the primitive non-centrosymmetric space groups the permissible origins are defined to be those points which are equivalent to at least one of the eight points