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A Determination of the Debye–Waller Temperature Factor and the X-ray Debye Temperature for Ni, Cr, Fe, Mo and W

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The integrated intensities of high-order reflexions for Ni, Cr, Fe, Mo, and W powder samples were measured at 296 and 77 °K with Mo $K\alpha$ radiation. The values 397 ± 6, 510 ± 6, 435 ± 6, 407 ± 6, and 333 ± 6 °K respectively were obtained for the Debye temperatures after correction for thermal diffuse scattering. These values are in good agreement with those calculated from force-constant models determined by inelastic neutron scattering.

Introduction

X-ray diffraction measurements provide several methods of determining Debye–Waller temperature parameters. One of the most commonly used is to measure the Bragg intensities at a fixed temperature and fit the obtained data with theoretical atomic scattering factors (f-curve fit). Although recent calculations for free-atom scattering factors can be considered rather reliable for this purpose, incorrect conclusions may ensue from experimental difficulties in separating the background scattering for the high-angle reflexions which, moreover, are partly overlapping. In the case of powder samples there will also be severe difficulties due to the effects of preferred orientation, porosity, surface roughness, and line broadening (*cf.* Paakkari, Suortti & Inkinen, 1970).

Another method is to study the temperature variation of a Bragg reflexion (or several reflexions). These measurements allow the elimination of experimental errors due to preferred orientation and grain size and theoretical atomic scattering factors are no longer needed. However, the temperature dependence or a reference value at some temperature of the X-ray Debye temperature, θ_M, must be obtained by an independent method in order to evaluate Debye–Waller parameters. Several authors (*cf.* Barron, Leadbetter, Morrison & Salter, 1966) indicate that the typical variation of $\theta_M(T)$ between 77 and 296 °K is likely to be much less than that of the heat-capacity Debye temperature, and an assumption of a constant value for θ_M for this temperature interval is in many cases rather good. Accordingly, many authors have applied this assumption to convert their results to the value of the X-ray Debye temperature (for example, Walford, 1969; Linkoaho, 1970). Another suggestion is to avoid large slopes in the low-temperature region in the plot of θ_M *versus* T, as presented by Chipman (1960).

Another approach to the problem is to calculate θ_M from a detailed experimental description of phonon states in a solid, obtained by inelastic scattering of neutrons or X-rays. These calculations are based on the harmonic approximation in the interatomic potential.

The purpose of the work described in this paper was to obtain information about the thermal parameters of some cubic metals by measuring Bragg intensities from powder samples at two temperatures ($T_1 = 77$ and $T_2 = 296$ °K). For all of these metals a θ_M value calculated from a force-constant model was available in the literature.

Theory

The integrated intensity of a Bragg reflexion depends on the specimen temperature through the Debye–Waller factor M, which is related to the Debye–Waller parameter B, by

$$M = B\kappa^2 = 8\pi^2\overline{u^2}\kappa^2, \tag{1}$$

where $\overline{u^2}$ is the mean-square displacement, perpendicular to the reflecting plane, of an atom due to its vibrational motion and $\kappa = \sin\theta/\lambda$. Because

$$f = f_0 \exp(-B\kappa^2), \tag{2}$$

where f_0 is the atomic scattering factor for an atom at rest, the temperature dependence of the Bragg intensity is obtained from

$$\ln\left[p\frac{I_{B1}}{I_{B2}}\right] = 2\kappa_2^2 B_2 - 2\kappa_1^2 B_1 \tag{3}$$

where p is a correction factor due to the thermal expansion of the crystal

$$p = \frac{F^2(\kappa_2)}{F^2(\kappa_1)}\frac{K(\theta)_1}{K(\theta)_2}. \tag{4}$$

The subscripts 1 and 2 refer to temperatures T_1 and T_2. F is the structure factor, $K(\theta)$ the Lorentz polarization factor and I_B the integrated Bragg intensity which has been corrected for thermal diffuse scattering (TDS). In terms of the Debye theory B is given by

$$B=\frac{6h^2T}{mk\theta_M^2}\left\{\frac{1}{x}\int_0^x\frac{u\mathrm{d}u}{e^u-1}+\frac{x}{4}\right\},\qquad(5)$$

where h is Planck's constant, k is Boltzman's constant, m is the atomic mass, and $x=\theta_M/T$.

The corrections for one-phonon TDS were made using a computer program by Walker (1972).

Experimental

The use of monochromatic radiation was found to be necessary to avoid the effect of absorption edges in the separation of background scattering. Radiation from a Mo anode was monochromated by a quartz crystal which was of the Johansson type. Mo $K\alpha$ radiation was selected to extend measurements to high values of κ where the intensities depend more sensitively on the value of B. The typical features of the powder samples used for the measurements are given in Table 1.

Table 1. *Properties of the samples used for the measurements*

	Purity (%)	Particle size (μm)	Pressure (kp/cm^2)	Measured *hkl*
Ni *A* (1)	99·7	3–5	1000	511, 333
B (2)	99·9	4–5	1000	642 553, 731
Cr *A*	99·2	3–5	1000	321
B (3)			1000	431, 510 611, 532 721, 633, 552 732, 651
Fe *A* (4)	99·5	3–5	10	431, 510
B (4)	99·5	3–5	1000	611, 532 710, 550, 543 721, 633, 552
Mo *A*	99·99	5	550	431, 510
B	99·99	5	1000	732, 651 831, 743, 750
W *A*	99·9	1	2000	321
B	99·9	1	7500	431, 510 532, 611 552, 633, 721 554, 741, 811

(1) Carbonyl nickel powder as was used in the International Powder Project. The powder was provided by Dr L. D. Jennings.
(2) Nickel sponge powder.
(3) Sample *A* was annealed 24 h at 440°C *in vacuo*.
(4) Carbonyl iron powder.

Samples were mounted on the cold finger of a Materials Research Corporation low-temperature attachment. The alignment of the diffractometer could be maintained within ±0·02° in 2θ. The accuracy of measuring the temperature difference was estimated to be better than ±1°K. The high-order reflexions, indicated in Table 1 for each material, were measured by a Siemens diffractometer with a scintillation counter. Because the measuring cycle was rather long, the incident beam was monitored with another scintillation counter placed at right angles to the beam to receive the radiation scattered from a Mylar sheet. A typical variation of the intensity of the primary beam was found to be less than 0·2% during a measuring cycle of two days. A punched-card programmer was used to carry out the intensity measurements as well as the background determinations at each termination point of 2θ scans of an average width of 4°. The effect of temperature on the positions of diffraction lines was carefully taken into account when determining the scanning limits.

Results and discussion

Table 2 gives the mean values of B_2–B_1 averaged over all measured reflexions for each sample. The error estimates are based on the counting statistics and are found to be of the same order as differences between the samples A and B of each material. The values of θ_M are calculated by assuming $\theta_{M1}=\theta_{M2}$ in equation (1). The values of $B(296)$ are the corresponding values of the parameter B at 296°K. The last column gives the change of $B(296)$ if one assumes that θ_{M1} is 3% smaller than θ_{M2}. It is found that this results in changes which are only about the same order as the statistical accuracy of the values of $B(296)$.

It is interesting to compare the obtained values of the Debye–Waller parameter or the corresponding Debye temperature with those resulting from a description of the phonon states by a force-constant model.

Table 2. *Experimental values of B and* θ_M

The values of B_2–B_1 are given for both samples and the given error limits of the mean are due to the counting statistics. ΔB indicates the effect of a change of θ_{M1} by 3%. This is included in the final error limits given for $B(296)$ and θ_M.

	B_2–B_1					
	A	B	Mean	ΔB	$B(296)$	θ_M
Ni	0·231	0·226	0·229±0·004	0·006	0·386±0·012	397±6
Cr	0·146	0·148	0·147±0·002	0·005	0·272±0·006	510±6
Fe	0·196	0·200	0·198±0·002	0·006	0·341±0·010	435±6
Mo	0·135	0·133	0·134±0·002	0·002	0·225±0·006	407±6
W	0·110	0·107	0·108±0·002	0·003	0·173±0·006	333±6

These models are based on measurement of the normal-mode frequencies of a crystal by the inelastic scattering of thermal neutrons or photons and the calculations are made within the framework of the Born–von Kármán theory. These kinds of calculations have been published for nickel by Barron & Smith (1966) and Feldman (1969), for chromium by Feldman (1970) and for iron, molybdenum and tungsten by Merisalo & Paakkari (1973). The comparison of these results with the present X-ray values and with other experimental work, available in the literature, is given in Table 3.

Table 3. *Comparison of the Debye temperature,* θ_M, *of* Ni, Cr, Fe, Mo *and* W *as determined by various methods*

The values given in parenthesis are calculated from the data given by authors assuming constant value of θ_M between 77–296 °K. The values marked with an asterisk (*) are given only for demonstration (for explanation see text). They have no physical meaning.

θ_M(°K)	Method and source
Nickel	
397 ± 6	This work
402–406	Calculations based on inelastic neutron scattering data. Barron & Smith (1966) and Feldman (1969)
390 ± 5	*f*-curve fit, single crystal. Diana *et al.* (1969)
406 ± 10	*f*-curve fit, powder method. Inkinen & Suortti (1964)
417 ± 12	X-ray diffraction at two temperatures, powder method. Linkoaho (1971)
410 ± 10 (398)	X-ray diffraction at various temperatures, single crystal. Wilson *et al.* (1966)
377 ± 4	Neutron diffraction, *f*-curve fit, powder method. Cooper (1969)
Chromium	
510 ± 6	This work
524	Calculation based on inelastic neutron scattering data. Feldman (1970)
545 ± 20 (525)	X-ray diffraction at various temperatures, single crystal. Wilson *et al.* (1966)
512	Model calculation based on elastic constants. Sharma, Semwal & Mehratra (1971)
Iron	
435 ± 6	This work
435–443	Calculations based on inelastic neutron scattering data. Merisalo & Paakkari (1973)
409 ± 9	*f*-curve fit, powder method. Herbstein & Smuts (1963)
419*	*f*-curve fit, powder method. This work
Molybdenum	
407 ± 6	This work
399	Calculation based on inelastic neutron scattering. Merisalo & Paakkari (1973)
Tungsten	
333 ± 6	This work
347	Calculation based on inelastic neutron scattering. Merisalo & Paakkari (1973)
377 ± 11	X-ray diffraction at two temperatures. Walford (1969)
316*	*f*-curve fit. This work, sample *A*
301*	*f*-curve fit. This work, sample *B*

There are several results for nickel. The present value is in good agreement with that calculated from the phonon dispersion measurements of Birgenau, Cordes, Dolling & Woods (1966) by Barron & Smith (1966) and by Feldman (1969). Also the earlier X-ray determinations (*f*-curve fit) at fixed temperature by Diana, Mazzone & DeMarco (1969) and by Inkinen & Suortti (1964) agree within the experimental error with the present value. The assumption of constant θ_M has also been used by Linkoaho (1971) for the temperature interval 300–4 °K but his result is somewhat greater than the present one. If the data given by Wilson, Skelton & Katz (1966) are treated assuming constant θ_M, they result in $\theta_M = 398$ °K. The present work does not support the neutron-diffraction work (*f*-curve fit) by Cooper & Taylor (1969) which indicated about 10% increase of the Debye–Waller parameter for Ni because of the anharmonicity of the lattice vibrations at room temperature.

Measurements on chromium are sparse. The present result is about 3% less than that calculated from the inelastic neutron scattering data (Feldman, 1970) and than that measured by Wilson *et al.* (1966) by X-ray methods at various temperatures using a single crystal.

For iron the calculations of θ_M based on various force-constant models are in agreement with the present result. For demonstration, more than ten high-angle reflexions of iron powder sample were taken into account to calculate a result 419 °K using a fit to the X-ray atomic scattering factor curve at the room temperature. It is suggested that the lower value of θ_M, which corresponds to a greater value of *B*, is due to the effect of line broadening in cold-worked powders, which results in too high values of background.

In the case of molybdenum, the present value is in essential agreement with the one calculated by Merisalo & Paakkari (1973) from the force-constant model given by Walker & Egelstaff (1969).

The present value for tungsten is about 4% less than that calculated from the force-constant model given by Chen & Brockhouse (1964). On the other hand, Walford (1969) reports $\theta_M = 377$, which differs by more than 10% from the present result, although obtained by the same method. Further, the failure of the method of the *f*-curve fit is demonstrated in the case of tungsten (Table 3). The value of *B* is found to increase as a function of moulding pressure.

By way of summary, the present experimental results agree within 4% of those calculated from the data obtained by inelastic scattering of neutrons. This agreement is very good in comparison, for example, with the range of various X-ray determinations of θ_M. It seems very evident that for these metals the approximation $\theta_{M1} = \theta_{M2}$ is reasonable between the temperatures 77 and 296 °K.

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Réduction de Moitié du Volume Mémoire et de la Durée de Calcul dans l'Usage des Algorithmes de Transformation de Fourier Rapide (FFT)

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After a brief review of the crystallographic Fourier transform problem, this paper compares three methods for its computer implementation with reference to core-storage capacity and computation time: the classic method, the simple Fast Fourier Transform algorithms and a new method. The first method needs, especially for a macromolecular three-dimensional structure, too many operations and therefore too long a computation time and poor accuracy. The remarkable FFT algorithm, on the other hand, leads to large savings in computation time with a better accuracy, but using no crystallographic symmetry wastes too much storage capacity. The third method, using FFT but taking into account Friedel's law by means of a simple *in situ* process, approximately halves the storage capacity as well as the computation time.

Introduction

Les calculs numériques radiocristallographiques requièrent généralement un stockage mémoire en ordinateur et un temps d'unité centrale notables, en particulier la transformation de Fourier conduite par les méthodes conventionnelles. Le nombre de données à traiter croissant en fonction de la complexité de la structure à étudier, il devient alors crucial de se poser la question de l'optimisation des calculs, notamment lors de l'étude de la structure tridimensionnelle des macromolécules.

L'usage des algorithmes de transformation de Fourier rapide ('Fast Fourier Transform' – FFT), (Cooley & Tukey, 1965), dans leur forme initiale fait déjà avancer de façon décisive le problème du calcul de la Transformation de Fourier Discrète (TFD), auquel est toujours conduit le cristallographe qui désire effectuer une transformation de Fourier continue. En effet, K étant le nombre de données, une réduction du temps de calcul proportionnelle à $\log_2 K/K$ par rapport à l'utilisation directe de la définition est obtenue, et cela quelle que soit la dimension de l'espace considéré: 1 pour les corps amorphes, 2 pour le calcul des projections tridimensionnelles, 3 pour le calcul des densités électroniques. Ce gain en temps de calcul, croissant très rapidement avec K, attira évidemment l'attention de certains chercheurs qui en recommandèrent l'emploi en radiocristallographie (Bondot, 1971; Lifchitz, 1971). (Voir l'Appendice pour quelques propriétés utiles de la TFD; le lecteur intéressé par la FFT pourra consulter avec intérêt Cochran *et al.* (1967) et les nombreux articles qui suivirent dans les revues de traitement du signal et d'informatique surtout aux U.S.A.)

Mais on doit constater que malgré tout la FFT reste encore trop peu utilisée par les cristallographes, peut-être parce qu'elle nécessite l'utilisation de valeurs numériques complexes et peut ainsi poser des problèmes