

Acta Cryst. (1965). 19, 487

Variation of the Debye parameter B with temperature. By K. LONSDALE and K. EL SAYED, *University College, London, W.C.1, England*

(Received 27 January 1965)

Independent studies of the crystal structure of anthraquinone $C_{14}H_8O_2$ have been made at five temperatures: $+20.5^\circ$, -12.5° , -72° , -112° and $-170^\circ C$; and anisotropic B parameters have been derived from the b_{ij} values at each temperature for each atom. Although the intensity measurements, and corrections for extinction *etc.* were made with care, they were not of the highest accuracy. Nevertheless it was clear that there was a steady decrease of the B parameters generally with decreasing temperature; and the ratio $\sqrt{\langle u^2 \rangle}(-170^\circ C)/\sqrt{\langle u^2 \rangle}(+20.5^\circ C)$ was found to vary only over a range of 0.49 to 0.72 for all atoms and all directions. Even the oxygen atoms, which were executing very large non-rigid-body vibrations normal to the molecular plane, gave ratios well within this range (0.59, 0.60, 0.60 for values along a , b , c^* respectively), showing that these independent vibrations were dependent on temperature in a way similar to that of the more nearly rigid-body vibrations of the anthracene nucleus.

It seemed to be of interest to compare the rate of change of \bar{B} with temperature with that of other compounds for which suitable thermal data were available at more than one temperature. In order to do so, all data were normalized to their room-temperature values, and values of $B/B(R)$ were then plotted against $T/T(\text{Room})(^\circ K)$ for these various substances (Fig. 1). It is interesting to see that the points all lie within fairly closely limiting curves. The values at very low temperatures for hexamethylene tetramine are particularly useful, as they demonstrate the probability that the curves swing round near to $0^\circ K$. The intercept on the B axis is a measure of the zero-point energy and of the frozen-in disorder. This is low for $C_{14}H_8O_2$, $C_6H_{12}N_4$, $C_{14}H_{10}$ and $C_{24}H_{20}$. For $C_{16}H_{16}$, benzil and α -quartz the

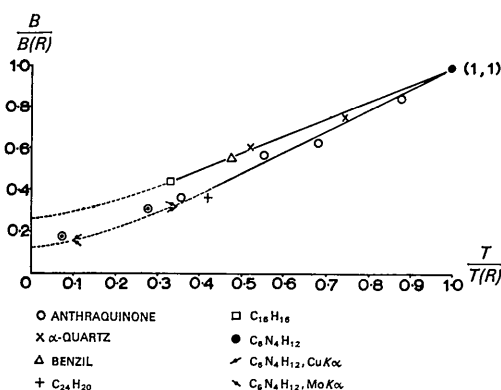


Fig. 1. The Debye coefficients for various metals normalized to the room-temperature values $B(R)$, plotted against the absolute temperature normalized to room temperature, and then extrapolated to $0^\circ K$. All data are for temperatures less than $T(R)^\circ K$. Sources of original data are as follows: anthraquinone, El Sayed (1965); α -quartz, Young & Post (1962); benzil, Brown & Sadanaga (1965); $C_{24}H_{20}$, Coppola (1964); $C_{16}H_{16}$, Lonsdale, Milledge & Rao (1960); $C_6N_4H_{12}$, Forrester (1961); $C_6N_4H_{12}$, Cu $K\alpha$ and $C_6N_4H_{12}$, Mo $K\alpha$, Becka & Cruickshank (1961).

value of $B(0^\circ K)$ relative to $B(R)$ may be at least twice as large.

Within the region $100^\circ K$ to $295^\circ K$, however, the relationship appears to be approximately linear and if more points could be obtained for such a curve for a number of substances this might be a good way of estimating the zero-point energy (if different specimens gave similar B data) or the amount of disorder present where different specimens of the same substance gave different graphs.

Figs. 2 and 3 show similar curves above room temperature for UO_2 and ThO_2 (Willis, 1963), the points for α -quartz also being given for comparison. The UO_2 and ThO_2 points both lie on well-defined curves which, if extrapolated without further flattening intersect the $0^\circ K$ ordinate at or above $0.5 B(R)$, indicating a large degree of zero-point energy or disorder. Willis (1963) has suggested that there is in these

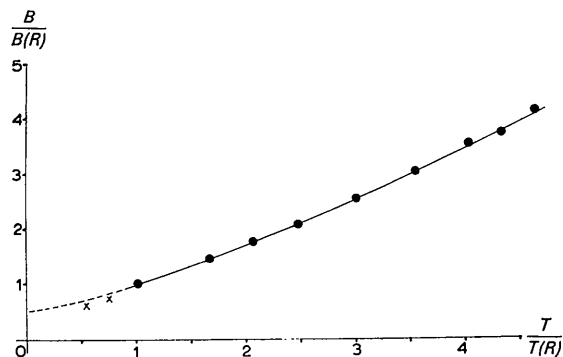


Fig. 2. Debye coefficients for uranium dioxide normalized to the room-temperature value $B(R)$, plotted against the absolute temperature normalized to room temperature, and then extrapolated to $0^\circ K$. The values actually used are $(B_U + 2B_0)$ but $(B_U + B_0)$ gives almost the same graph (Willis, 1963). Two points for α -quartz are also shown.

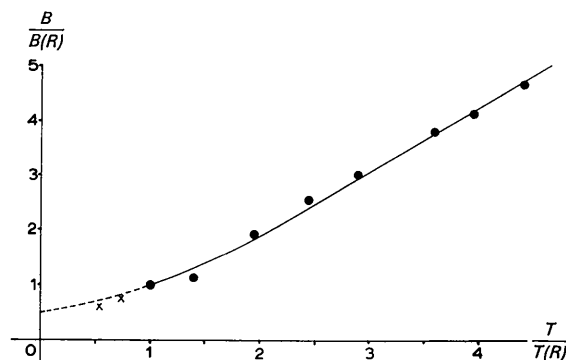


Fig. 3. Debye coefficients for thorium dioxide normalized to the room-temperature value $B(R)$, plotted against the absolute temperature normalized to room temperature, and then extrapolated to $0^\circ K$ (Willis, 1963). The values used are $(B_{Th} + 2B_0)$. $(B_{Th} + B_0)$ gives almost the same graph. Two points for α -quartz (Young & Post, 1962) are added.

fluorite-type structures a considerable measure of relaxation of the oxygen positions and this is confirmed by the curves, or at least would explain them.

References

- BECKA, L. N. & CRUICKSHANK, D. W. J. (1961). *Acta Cryst.* **14**, 1092.
 BECKA, L. N. & CRUICKSHANK, D. W. J. (1963). *Proc. Roy. Soc. A*, **273**, 435.

- BROWN, C. J. & SADANAGA, R. (1965). *Acta Cryst.* **18**, 158 and private communication.
 COPPOLA, J. (1964). Thesis (London).
 EL SAYED, K. (1965). Thesis (London).
 FORRESTER, J. D. (1961). Thesis (London).
 LONSDALE, K., MILLEDGE, H. J. & RAO, K. V. K. (1960). *Proc. Roy. Soc. A*, **255**, 82.
 WILLIS, B. T. M. (1963). *Proc. Roy. Soc. A*, **274**, 134.
 YOUNG, R. A. & POST, B. (1962). *Acta Cryst.* **15**, 337.

Acta Cryst. (1965). **19**, 488

Gitterkonstanten von Fe-Mo-Legierungen mit Mo-Gehalten bis 20 Gew.-Prozent. Von A. FUCHS und

B. ILSCHNER, *Institut für Metallphysik der Universität Göttingen, Deutschland*

(Eingegangen am 26. Januar 1965)

Für eine Untersuchung der Ausscheidungskinetik im binären System Fe-Mo (Fuchs, 1965) wurde eine Reihe von Legierungen hergestellt, über deren Gitterparameter nachstehend berichtet wird.

Presslinge aus entsprechenden Mischungen von reinem Fe- und Mo-Pulver wurden 3 h im Wasserstoffstrom bei 1000°C gesintert, in Al₂O₃-Tiegeln unter Vakuum (<10⁻³ Torr) im Induktionsofen geschmolzen und in Gusseisenkokillen vergossen. Der Mo-Gehalt der Gusstangen wurde mittels Röntgenfluoreszenzanalyse ermittelt (siehe Tabelle 1). Die typischen Verunreinigungen der Legierungen sind in Tabelle 2 aufgeführt. Auf Scheiben (10 mm Ø, 2 mm dick) der zu untersuchenden Legierung wurden jeweils Feilspäne (≤80 µm) derselben Legierung gebracht und bei 1350°C unter Wasserstoff und Argon (ca. 1:10) in 2 h aufgesintert. Damit das Molybdän in den übersättigten Legierungen (>6 Gew. % Mo) gelöst blieb, wurden diese Proben in Wasser abgeschreckt. Das Aufsintern von Pulver hatte den Zweck, möglichst feinkörnige Proben für die röntgenographische Untersuchung zu erhalten.

Die Gitterkonstanten wurden im fokussierenden Rückstrahlverfahren bestimmt, wobei Probe und Film gedreht werden konnten. Zur Eichung wurde eine Suspension von Goldmehl (Fa. Degussa) in Öl auf die Probe gebracht. Bei Verwendung von Co K α -Strahlung wurden die Ringe des 310-Reflexes des Eisenmischkristallgitters und des 420-Re-

flexes des Goldgitters vermessen. Der maximale Fehler beträgt ±0,0005 Å. Die Gitterkonstanten sind in Tabelle 1 enthalten und in Fig. 1 in Abhängigkeit vom Mo-Gehalt dargestellt. Der gemessene Wert für Reinst Eisen stimmt innerhalb der Fehlergrenzen mit dem Literaturwert (Pearson, 1958) (2,8664 Å) überein. In Fig. 1 sind ferner Messwerte anderer Autoren zum Vergleich eingetragen.

Die Analysen für Tabelle 2 wurden im Max-Planck-Institut für Eisenforschung, Düsseldorf, durchgeführt, wofür wir Herrn Prof. Dr. phil. W. Oelsen vielmals danken. Der Deutschen Forschungsgemeinschaft sind wir für die Bereitstellung von Sachmitteln zur Durchführung dieser Arbeit zu Dank verpflichtet.

Literatur

- ELSEN, G. & WASSERMANN, G. (1961). *Z. Metallk.* **52**, 263.
 FUCHS, A. (1965). Dipl.-Arbeit, Univ. Göttingen.
 GULJAEV, A. P. & TRUSOVA, E. F. (1950). *Z. Tekh. Fiz. SSSR*, **20**, 66, zitiert nach Pearson (1958), S. 635.
 HORNOGEN, E. (1961). *Z. Metallk.* **52**, 47.
 PEARSON, W. B. (1958). *Handbook of Lattice Spacings and Structures of Metals and Alloys*, S. 625.

Tabelle 1. Mo-Gehalt der Legierungen und Gitterkonstanten

Leg. Nr.	Gew. % Mo	At. % Mo	Gitterkonstante, 20°C
0	0	0	2,8665 Å
1	2,1	1,25	2,8708
2	4,0	2,38	2,8753
3	7,0	4,22	2,8815
4	9,9	6,06	2,8889
5	12,5	7,73	2,8932
6	14,9	9,30	2,8990
7	19,8	12,55	2,9098

Tabelle 2. Typische Verunreinigungen

Leg. Nr.	Mo	C	Mn	Ni	Si	Al	N ₂
3	7,09	0,004	0,002	0,005	≤ 0,01	0,003	0,001
6	14,90	0,003	0,012	0,007	≤ 0,01	0,006	0,002

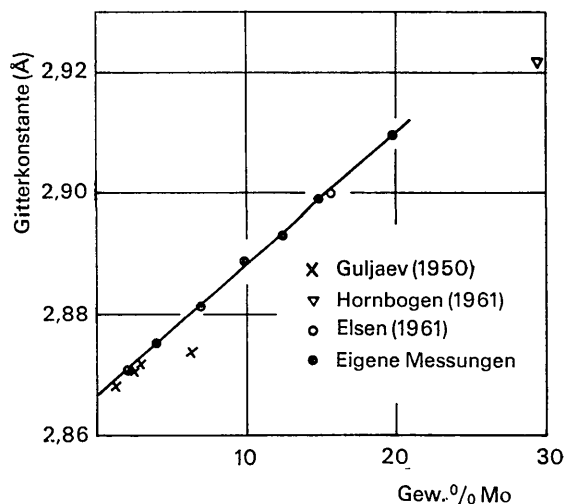


Fig. 1. Gitterkonstanten von Fe-Mo-Legierungen.