

Table 9 (cont.)

$\sin \theta/\lambda$ (\AA^{-1})	Input values	Calculated values
0.25	0.5625	0.5622
0.30	0.4507	0.4499
0.35	0.3524	0.3519
0.40	0.2696	0.2697
0.45	0.2018	0.2024
0.50	0.1475	0.1482
0.60	0.0719	0.0718
0.70	0.0282	0.0273
0.80	0.0047	0.0041
0.90	-0.0068	-0.0066
1.00	-0.0116	-0.0110
1.10	-0.0128	-0.0126

Table 10. Input data and corresponding calculated values for the $\langle j_4 \rangle$ Fe⁺ scattering function

$\sin \theta/\lambda$ (\AA^{-1})	Input values	Calculated values
0.05	0.0001	0.0000
0.1	0.0014	0.0012
0.2	0.0142	0.0144
0.3	0.0379	0.0380
0.4	0.0608	0.0601
0.5	0.0767	0.0763
0.6	0.0847	0.0853
0.7	0.0862	0.0871
0.9	0.0772	0.0761
1.1	0.0623	0.0627

References

Tables 9 and 10 give the input data and the equivalent values for the two examples; the $\langle j_0 \rangle$ form for Fe²⁺ and the $\langle j_4 \rangle$ form for Fe⁺.

One of us (EJL) wishes to thank the Science Research Council for the award of a studentship during the tenure of which this work was completed. The fitting of the asymmetric curves was carried out on the University of London C.D.C. 6600 computer.

- BLUME, M., FREEMAN, A. J. & WATSON, R. E. (1962). *J. Chem. Phys.* **37**, 1245.
 FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.
 HOSOYA, S. & SATAKA, S. (1963). *Technical Report of ISSP*, Ser. B. No. 5, The Institute for Solid State Physics, Univ. of Tokyo, Tokyo, Japan.
 HOSOYA, S. & SATAKA, S. (1964). *Technical Report of ISSP*, Ser. B. No. 6, The Institute for Solid State Physics, Univ. of Tokyo, Tokyo, Japan.
 WATSON, R. E. & FREEMAN, A. J. (1961). *Acta Cryst.* **14**, 27.

Acta Cryst. (1971). A27, 549

Lattice Parameters and Thermal Expansion Coefficients of Al, Ag and Mo at Low Temperatures. Comparison with Dilatometric Data*

BY M. E. STRAUMANIS AND C. L. WOODARD†

*Department of Metallurgical Engineering and Graduate Center for Materials Research,
University of Missouri-Rolla, Rolla, Missouri 65401, U.S.A.*

(Received 29 October 1970)

Lattice parameters and thermal expansion coefficients of Al, Ag and Mo were determined at temperatures between 30 and 180°K in a special X-ray camera without the use of liquid gases. The powder samples were cooled by a mechanical refrigerator, and symmetrical back-reflections patterns of the three metals were prepared. The purpose was to check the reliability of this method by comparing the lattice parameters and expansion coefficients calculated from X-ray patterns with those obtained by other well established, interferometric-dilatometric methods. The expansion coefficients were reproduced with reasonable precision, but the lack of reliable measurements of low-temperature parameters in the literature prevented a conclusion from being reached concerning the accuracy of the lattice parameters calculated. Values of the expansion coefficients and the lattice parameters are given.

The aim of the present investigation was to determine, with high precision, the lattice parameters of crystal-line substances at low temperatures without the use of liquid gases for sample cooling. The powder sample (grain size about 20 μ) was placed on a silver sample

holder, tightly screwed to the cold head of a cooling machine. A symmetrical back-reflection vacuum camera provided the vacuum shroud for the cold head. The high-angle interference were registered on a film (on which six exposures can be made) fastened in a movable cylindrical film holder within the camera. Lattice-parameter determinations between 30 and 180°K were possible. Since more advanced refrigerators are now available, temperatures as low as 3.6°K (according manufacturers, claims), can be reached. The camera for

* Presented in part at the Tuscon meeting of the ACA, February 1968. Contribution No. 113 from the Materials Research Center.

† Present address: Department of Industrial Engineering, Kansas State University, Manhattan, Kansas 66501, U.S.A.

making low-temperature lattice-parameter determinations is described by Woodard & Straumanis (1971).

At first it was necessary to compare the lattice parameters obtained here with those established by well known methods using liquid gases as coolants. The only suitable article we found was that of Figgins, Jones & Riley (1965) on aluminum.

Powder from 99.999% pure aluminum could not be prepared because of the ductility of the metal. Therefore, a powder of 99%+ purity (Pierce Chemical Company, Rockford, Illinois) of a particle size from 8 to 15 μ , had to be used. Good back-reflection patterns were obtained with Cu radiation ($\text{Cu } K\alpha_1 = 1.54051 \text{ \AA}$) during 30 minutes of exposure. The refraction correction of 0.00003 \AA (Guinier, 1945) was added to the calculated constants (Jette & Foote, 1935). The lattice parameters and the thermal expansion coefficients α versus the temperature are plotted in Fig. 1.

Fig. 1 shows that the three curves of lattice parameter a versus temperature are similar in shape, although the absolute values of the lengths of the cube edges differ significantly. This is probably due to variations in the purity of the Al samples. Lattice constants calculated on the basis of a at 273°K from expansion coefficients α , obtained by interferometric methods by

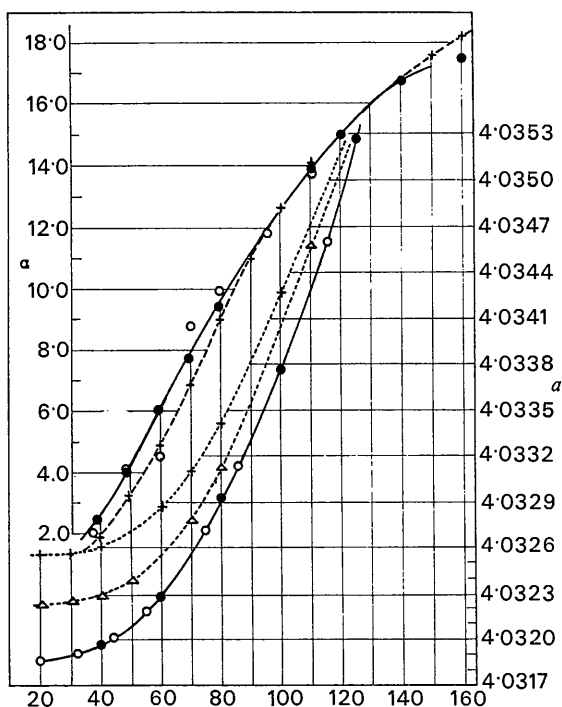


Fig. 1. Lattice parameters (\AA) and thermal expansion coefficients ($\alpha \cdot 10^6 \text{K}^{-1}$) versus temperature ($^\circ\text{K}$). Lattice parameters a of aluminum obtained by X-ray technique (right):
 ○ Figgins, Jones & Riley (1965), using liquid gases
 ● Present, and calculated from expansion coefficients α obtained by
 + Gibbons (1958) from interferometric measurements,
 △ Bijl & Pullman (1955) from capacitance measurements.
 Thermal expansion coefficients α versus temperature T (left).

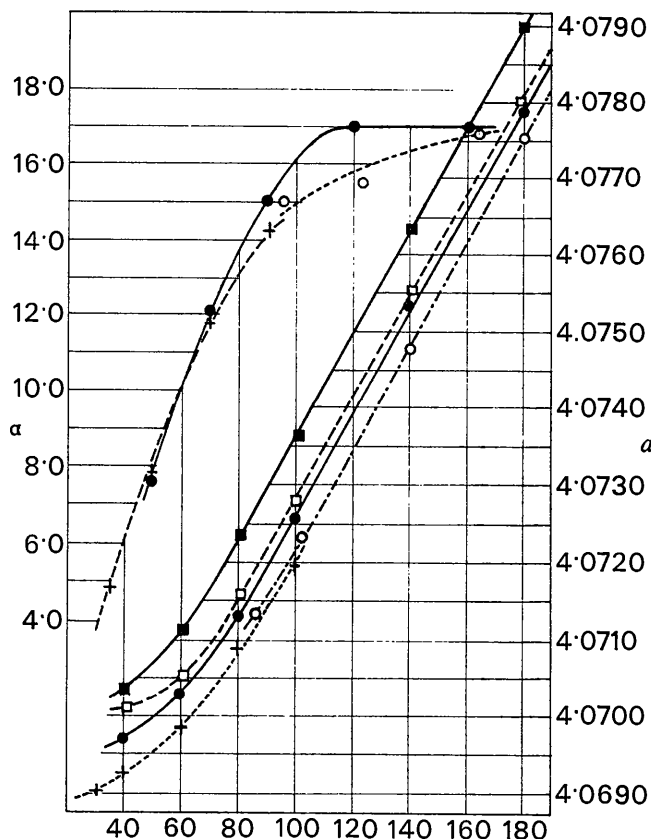


Fig. 2. Expansion coefficients α in 10^6K^{-1} (left) and lattice parameters a in \AA (right) of Ag at low temperature in $^\circ\text{K}$ (refr. corr. of +0.00019 \AA is added).
 ○ Data of Nix & MacNair (1942), α and a (calc. from interferometric α).
 + Data of Frazer & Hallett (1965), α and a (calc. from interferometric α).
 ■ Present a of the massive, fine grained 99.99% Ag sample holder, X-ray work.
 □ Present a of 99.7% Ag powder, embedded in vaseline, X-ray.
 ● Present a and α for 99.7% Ag-powder embedded in In, X-ray work.

Gibbons (1958) and Bijl & Pullman (1955), are higher. The equation that represents the present measurements on Al (a in \AA versus $^\circ\text{K}$) is as follows:

$$a_t = 4.03 + 2.11918 (10^{-3}) - 1.66133 (10^{-5})T + 2.83407 (10^{-7})T^2 + 9.89808 (10^{-10})T^3 - 4.82768 (10^{-12})T^4, \quad (1)$$

where a_t is the lattice parameter at the temperature T . The first derivative of equation (1) gives the slope of the curve at the temperature T . The thermal linear coefficient of expansion α is then

$$\alpha = da_t/dT \cdot a_{t_0}, \quad (2)$$

where a_{t_0} is the lattice parameter at 273°K. The results are also summarized in Fig. 1.

In all cases α rapidly approaches zero with falling

temperature. The values of α derived from lattice-parameter measurements agree well, while those calculated from dilatometric (interferometric) data are slightly lower.

No low-temperature lattice-parameter measurements of Ag and Mo could be found in the literature. The results of the present measurements on Ag are shown in Fig. 2. The Ag powder (purity 99.7%, probably containing some Cu and Mg) was embedded (for better heat conductance) in a thin In layer which adhered well to the Ag sample holder. This time, the lattice parameters calculated from dilatometric values of α , using $a = 4.08435 \text{ \AA}$ for Ag at 273°C as a reference point, are lower than those measured here. However, the expansion coefficients are in good agreement below about 70°K (Fig. 2).

The same applies to Mo, as illustrated in Fig. 3. The a values from dilatometric-interferometric data were calculated on the basis of $a = 3.14673 \text{ \AA}$ at 273°K (Straumanis & Shodhan, 1968).

Finally, there is the question of the temperature of the sample irradiated by X-rays. At room temperature the lattice parameter is not affected by the heat of the X-rays within the error limits. However, at very low temperatures, where heat capacity of the crystalline

samples becomes very small, the heat produced by X-ray absorption may increase the temperature of the substance's outer layers considerably. This increase might not be noticed by the measuring instruments. In this connection a phenomenon described by Mendelssohn (1966) should be mentioned where the temperature of the sample was increased by the heat produced by the vibration of nylon threads holding the sample. Therefore, some measurements of lattice parameters were made by using (1) a massive, fine-grained sample holder consisting of 99.99% Ag, (2) an Ag powder (99.7% pure) embedded in vaseline adhering to another Ag sample holder and (3) the same Ag powder embedded in an In foil on the same holder. The results as shown in Fig. 2 indicated that in the first and last case, where the heat flow was excellent, the lattice parameter of Ag, starting at 60°K , decreased faster with decreasing temperature than in the second case where the heat conductivity was hampered by the vaseline. At 40°K the difference was about 0.0004 \AA and might be attributed to the heating effect of the X-rays. Although the lattice parameters of the sample holder of high purity Ag (99.99%) were somewhat higher, the $a^\circ(\text{K})$ curves of this and the third sample ran nearly parallel, indicating that the purity of the sample affected the expansion coefficients only slightly.

The measurements show that this method of determining lattice parameters at low temperatures works well, especially in finding the expansion coefficients. As there is some doubt concerning the absolute value of the lattice parameters, a further investigation with other substances is presently under way.

Thanks are expressed to Dr W. J. James, Director of the Materials Research Center, for assistance with the manuscript.

References

- BIJL, D. & PULLMAN, H. (1955). *Physica*, **21**, 285.
 CORRUCINI, R. J. & GNIEVEK, J. J. (1961). *Thermal Expansion of Technical Solids at low Temperatures*, p. 1. NBS Monograph.
 FIGGINS, B. F., JONES, G. O. & RILEY, D. P. (1965). *Phil. Mag.* **1**, 747.
 FRAZER, D. B. & HALLET, A. C. H. (1965). *Canad. J. Phys.* **43**, 193.
 GIBBONS, D. F. (1958). *Phys. Rev.* **112**, 136.
 GUINIER, A. (1945). *La Radiocristallographie*, p. 6. Paris: Dunod.
 JETTE, E. R. & FOTTE, F. (1935). *J. Chem. Phys.* **3**, 605.
 MENDELSSOHN, K. (1966). *The Quest for Absolute Zero*, p. 175. New York: McGraw-Hill.
 NIX, F. C. & MACNAIR, D. (1942). *Phys. Rev.* **61**, 74.
 STRAUMANIS, M. E. & SHODHAN (1968). *Tr. Met. Soc. AIME*, **242**, 1185.
 WOODARD, C. L. & STRAUMANIS, M. E. (1971). *J. Appl. Cryst.* **4**, 201.

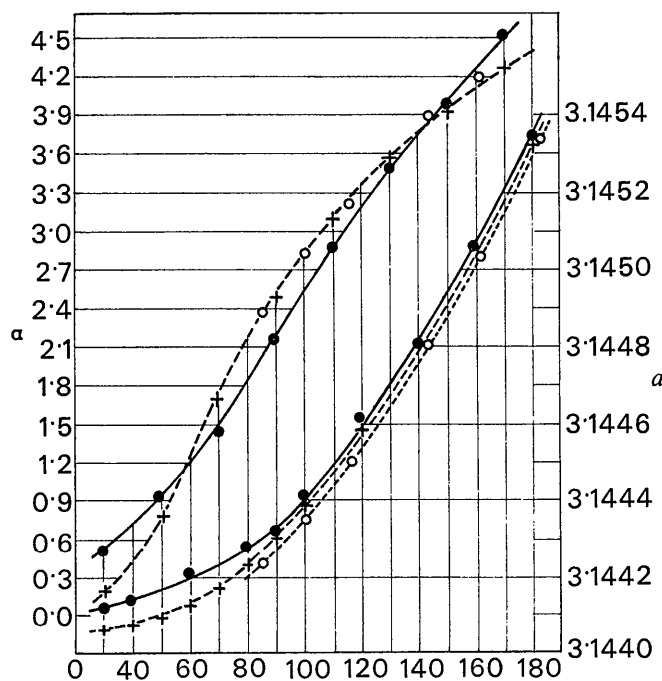


Fig. 3. Expansion coefficients α (10^{-6}K^{-1}) and lattice parameters a (\AA) of Mo at low temperature. Refraction correction of $+0.00010 \text{ \AA}$ added.

- Data of Nix & MacNair (1942), interferometric work,
- + Data of Corruccini & Gnievek. (1961), compiled from the literature, and extrapolated values.
- Present, a and α , X-ray work.