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The Characteristic Temperature of Silver, Gold, Platinum and Lead from X-ray Reflexions*

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The characteristic temperature Θ and its dependence on temperature for silver, gold, platinum and lead were studied by measuring the variation with temperature of the intensity of X-ray reflexions from flat powder samples. For silver and platinum the measurements were in the range 100–700 °K, for gold 100–800 °K, and for lead 100–500 °K.

The value of Θ at room temperature was found to be 212 ± 7, 177 ± 5, 236 ± 5 and 85 ± 6 °K for silver, gold, platinum and lead respectively. For gold and platinum the dependence of Θ on temperature can be described by the thermal expansion alone while for silver and lead the measurements show a greater decrease of Θ with temperature.

Introduction

The temperature dependence of the intensity of the X-ray Bragg reflexions from solids can be described by the Debye–Waller factor $\exp(-2M)$, which contains the characteristic temperature Θ, a parameter characteristic of the material. The measured intensities, however, do not follow exactly the Debye–Waller theory, owing to the difference between the Debye spectrum and the real one. This difference can be taken into account by assuming that the parameter Θ depends upon temperature.

The present paper describes measurements of the integrated intensity of several reflexions of the f.c.c. metals silver, gold, platinum and lead; these measurements lead to a determination of their characteristic temperature and its dependence on temperature. Similar measurements on these metals have been carried out by other investigators. However, some of these were made with only one reflexion line, or were restricted to temperatures above ambient, or the results were treated by unsatisfactory methods for calculating Θ. Consequently, a more thorough investigation of Θ and its dependence on temperature was desirable.

Experimental

The measurements were carried out with a Philips X-ray diffractometer with the use of Cu $K\alpha$ radiation and a Geiger counter.

The samples were heated in a vacuum chamber by contact with a block of copper hard-soldered to an electric oven, which was mounted on the axis of the goniometer. A thermocouple in a small hole in the block was used to control the temperature. The samples were cooled in a second vacuum chamber with solid carbon dioxide and liquid air.

The temperature of the sample was determined from the measured peak shift and the accurately known thermal expansion relations. The error in temperature was estimated to be about ±3 °C.

Measurements on silver, gold and platinum were carried out on chemically precipitated powders, while for lead, 250 and 400 mesh filings were used.

The metal powder was mixed with a small amount of Aquadag and dried in a flat copper receptacle suitable for mounting on the metallic block of the chambers. Standard back-reflexion exposures were made before heating in order to ascertain whether the samples were sufficiently microcrystalline. The samples were then annealed in vacuum at a temperature higher than the highest temperature of measurements. The interesting reflexions were chart-recorded during the annealing, which was stopped when no more sharpening of the reflexion lines was observed. Exposures taken at the end of the high temperature measurements showed that the samples remained sufficiently microcrystalline, except for lead and possibly gold, where the films revealed the presence of some large crystallites. In all cases, however, no noticeable sharpening of the reflexion lines was observed.

The measured reflexion lines were 331, 420, 422 and 531 for silver, gold and platinum and 331, 420, 422, 511–333, 531, 600–442 for lead.

The measurements were made at a number of temperatures successively. In the high-temperature measurements each line was measured separately in the whole temperature range, except when small overlapping of two lines occurred. In the low temperature measurements the lines were measured one after the other at each temperature. The procedure was repeated for both temperature ranges in several runs.

The intensities were chart-recorded, with the angular velocity of the Geiger arm choosen so as to restrict the statistical error without extending excessively the duration of measurements.

The recorded reflexion lines were planimetered assuming a straight line background. The resulting areas

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represent the integrated intensity in arbitrary units (P). In cases of a pair of lines, such as 331–420, where a small overlapping of the wings occurred, it was found that the uncertainty in the separation of the two lines could not affect P by more than 1–2%. P was reproducible at room temperature to within 1–2% for silver, gold and platinum and 3–7% for lead.

Methods of calculating Θ

The measured integrated intensity of a reflexion line from a flat powder specimen of a f.c.c. metal is given by the formula:

$$P=C\,.\,B\,.\exp\left\{-\frac{12h^2}{mk}\,.\,(1-\beta)\,.\,\frac{\sin^2\theta}{\lambda^2}\,.\,\frac{T\Psi}{\Theta^2}\right\}\qquad(1)$$

where $\Psi=\Phi(x)+x/4$ and C is a constant independent of Bragg angle and temperature T. The factor B is given by:

$$B=N\,.\,p\,.\,f^2\,.\,\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}$$

The quantity $(1-\beta)$ takes into account the one phonon thermal diffuse scattering contribution (T.D.S.) to the measured intensity according to Chipman & Paskin (1959). According to these authors the relation between the measured integrated intensity P and the intensity P' that would be obtained in absence of T.D.S. is given by the formula:

$$P=P'\,.\,(1+2M\beta)$$

or because of the small value of $2M\beta$

$$P=P'\,.\,e^{2M\beta}\,.$$

The quantity β (for the f.c.c. crystals) is given by the expression:

$$\beta=\tfrac{1}{2}\,.\left(\frac{\pi}{3}\right)^{\frac{1}{3}}\,.\,\frac{a\cos\theta}{\lambda}\,.\,\Delta$$

where a is the lattice constant and Δ the length of the straight line background expressed in radians. The other symbols in the above equations have the same meaning as in James (1958).

The common method of determination of Θ from equation (1) is to eliminate the constant C which contains the unknown proportionality factor between the absolute value of the integrated intensity and its measured value in arbitrary units.

The constant C can be eliminated either by considering P as a function of $\sin^2\theta/\lambda^2$ for a given temperature (method A), or as a function of T for a given $\sin^2\theta/\lambda^2$, *i.e.* for a given reflexion line (method B).

Method A

According to equation (1) the plot of $\ln(P/B)$ as a function of $(1-\beta)\,.\,\sin^2\theta/\lambda^2$ for each temperature is a straight line with slope

$$-\frac{12h^2}{mk}\,.\,\frac{T\Psi}{\Theta^2}\,.$$

From this Θ can be calculated.

Method B

By applying equation (1) at temperatures T, T_0 we obtain:

$$R\equiv\frac{mk}{12h^2}\,.\,\frac{\lambda^2}{(1-\beta)\sin^2\theta_0}\,.\left\{\ln\frac{P}{P_0}-\ln\frac{B}{B_0}\right\}$$

$$=\frac{T_0\Psi_0}{\Theta_0^2}-\frac{T\Psi}{\Theta^2}\,.\,\frac{\sin^2\theta}{\sin^2\theta_0}\qquad(2)$$

where the subscript zero denotes the corresponding value at room temperature T_0.

To calculate Θ from equation (2), either the value Θ_0 is required, or some additional relation between Θ and Θ_0 must be known. In the present work the following assumptions concerning the additional relation were made.

B(i). If the temperature dependence of Θ is due to the volume expansion only, Θ_0 can be determined by using the relation $\Theta\{V(T)\}$. Of the various nearly equivalent treatments of Owen & Williams (1947), Zener & Bilinsky (1936) and Paskin (1957) the last was used. According to this plot of R *versus* T', where T' is a reduced temperature, should be a straight line. From the slope of this line Θ_0 and hence Θ can be determined.

B(ii). Another way of estimating Θ_0 and hence Θ *versus* T is that used by Chipman (1960). Using the fact that Θ *versus* T curves as determined from the elastic constants are approximately linear, one plots a family of Θ *versus* T curves, giving Θ_0 a series of arbitrary values, and selects the curve with smallest curvature.

B(iii). A different procedure proposed by one of the authors (S.M.) is based on the relation:

$$\Theta^{-2}=a\,.\,(1+\mu T)\qquad(3)$$

found by Maradudin & Flinn (1963), who considered the effect of the anharmonicity of the lattice vibrations on the Debye–Waller factor. The quantities a and μ are constants independent of temperature. It should be noted that equation (3) holds only for $T>\Theta$.

Application of equation (3) at T and T_0 gives:

$$\frac{\Theta^2}{\Theta_0^2}=\frac{1+\mu T_0}{1+\mu T}\,.\qquad(4)$$

By inserting equation (4) into (2) and rearranging we obtain:

$$\frac{R}{T_0-T+\tau_1}=\frac{1}{\Theta_0^2}+\frac{\mu}{\Theta_0^2(1+\mu T_0)}\,.\,(T+\tau_2)\qquad(5)$$

where τ_1, τ_2 are minor corrections resulting from the presence of $\sin^2\theta/\sin^2\theta_0$ in the right hand side of equation (2). (See appendix).

The plot of $R/(T_0-T+\tau_1)$ against $T+\tau_2$ must be a straight line with intercept $1/\Theta_0^2$ and slope $\mu/\Theta_0^2(1+\mu T_0)$. Thus Θ_0 and hence Θ *versus* T can be found.

The advantage of method A is that it gives the Θ values without any additional assumption concerning the relation Θ *versus* T. However, this method is very sensitive to any factor which has a different influence on the integrated intensity of the various reflexion lines. Such factors are: extinction, preferred orientation, misalignment of the specimen. In addition, the values of the atomic scattering factor *f*, which enter critically, are not sufficiently well known.

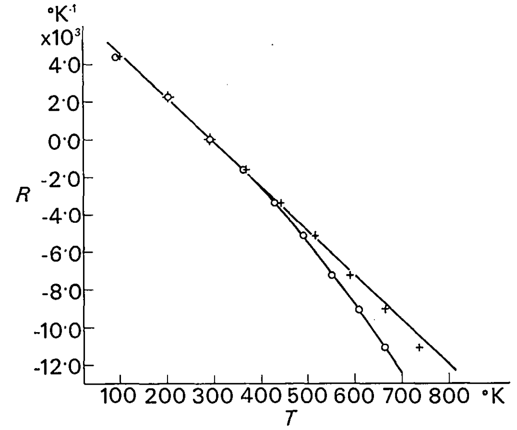

Fig. 1. Temperature dependence of the quantity R for silver. ○ R *versus* absolute temperature T. + R *versus* the reduced temperature T'.

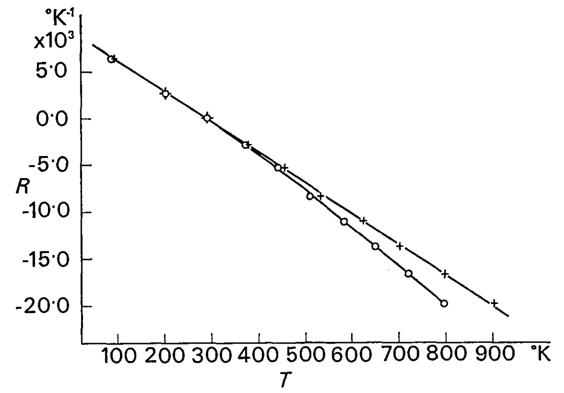

Fig. 2. Temperature dependence of the quantity R for gold. ○ R *versus* absolute temperature T. + R *versus* the reduced temperature T'.

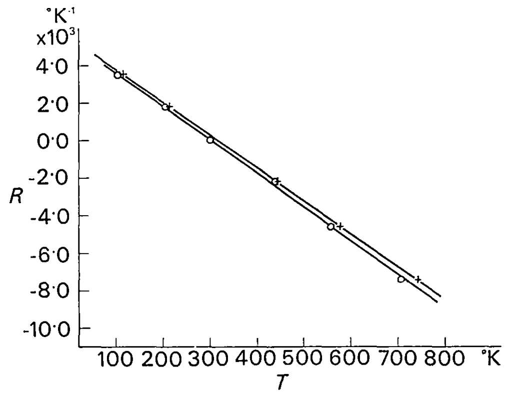

Fig. 3. Temperature dependence of the quantity R for platinum. ○ R *versus* absolute temperature T. + R *versus* the reduced temperature T'.

Method *B*, on the other hand, uses the ratio P/P_0 which is much less sensitive to extinction and almost independent of preferred orientation, misalignment and atomic scattering factor. The weak point of method *B* is the inevitable acceptance of an additional relation between Θ and T. Thus the calculated Θ values depend on the reliability of the Θ *versus* T relation.

Results and discussion

The experimental data of the present work were treated according to the methods described in the previous section. Concerning method *B* the calculations were carried out with the mean value of R from all measured reflexion lines. This quantity *versus* T is represented by circles in Figs. 1, 2, 3 and 4 for silver, gold, platinum and lead respectively.

According to equation (2) the quantity R at a given temperature must have the same value for all reflexion lines, if Θ is to be independent of the reflexion line. This was found to be so for platinum, while for silver and gold there are some systematic differences between the measured reflexion lines, but these are of the same order as the experimental errors. In the case of 250-mesh lead these differences are larger than the errors. Such large differences were also found from measurements on the 400-mesh specimen, taken in order to verify whether the results of the 250 mesh specimen were due to the coarseness of the sample. However, the differences are not similar, in the sense that the same reflexion line does not give the same R from the two specimens.

The results of the calculation of Θ are given in Table 1 in terms of Θ_0, the value of Θ at room temperature, and $\Delta\Theta/\Delta T$, the mean variation of Θ with temperature. The reported values for method *A* are those obtained from the measurements below T_0. The results obtained from measurements above T_0 were quite unreliable. This is mainly due to the fact that the

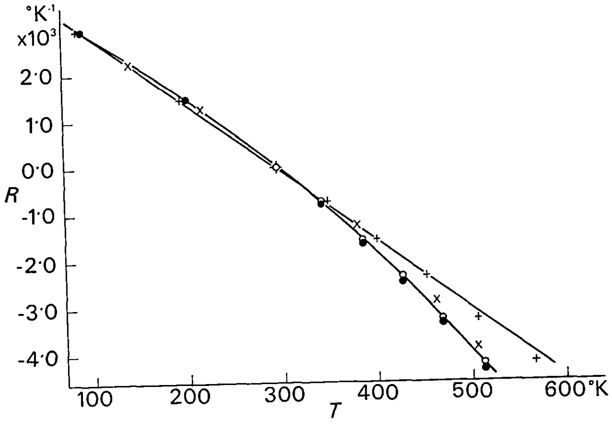

Fig. 4. Temperature dependence of the quantity R for lead. × and ● R *versus* absolute temperature T for 400 and 250 mesh specimens respectively. ○ and + the mean value of R *versus* absolute temperature T and the reduced temperature T' respectively.

sequence of the measurements in the high temperature region described in the experimental part is suitable for method *B* but not for method *A*. In fact between the measurement of two reflexion lines gradual changes in the specimen may occur, which affect the ratio of the intensities of the lines at a given temperature (method *A*), much more than the ratio of the intensities of the same line at two temperatures (method *B*).

The results obtained from methods *B*(i), *B*(ii) and *B*(iii) are in agreement within the experimental errors, while the values obtained from method *A* agree only for platinum, presumably owing to the previously discussed systematic errors inherent in method *A*.

Referring to the variation of Θ with temperature, the calculated values of $\Delta\Theta/\Delta T$ from methods *B*(i), *B*(ii), and *B*(iii) agree for gold and platinum, while for silver and lead methods *B*(ii) and *B*(iii) showed a stronger decrease of Θ with temperature than that expected from the volume expansion only. It should be noted that according to the method *B*(i), the plot of R *versus* T' must be a straight line. For gold and platinum this quantity showed a satisfactory linear behaviour with T' in the whole temperature range, while for silver and lead there is a downward curvature from linearity at higher temperatures, indicated by crosses in the figures. This behavior indicates that for gold and platinum the decrease of Θ with temperature can be described by the volume expansion alone while for silver and lead the decrease is larger than would be expected from the volume expansion.

Taking into account the merits of each method, we give in Table 2 the values of Θ which we consider as the most reliable. In the same table the corresponding results found from X-ray measurements by other authors are reported.

Andriessen (1935) and Boskovits , Roilos, Theodossion & Alexopoulos (1958) published results for silver; their values, however, were calculated on the incorrect assumption that either Θ is independent of temperature or that the application of formula (2) for a pair of temperatures, without considering the change of Θ, leads to the mean value of Θ in this region of temperatures. The values reported in Table 2 are obtained after applying method *B*(i) to their experimental data.

The reported values of Spreadborough & Christian (1959) and Haworth (1960) were obtained by the same method *B*(i), which they found to fit their data very well up to very high temperatures. Most of the above values agree with the result $\Theta_0 = 206\,^{\circ}\mathrm{K}$ from the present experimental data treated by method *B*(i) although, as mentioned, we obtain a systematic misfit for this method (see Fig. 1).

Herbstein (1961) reinterpreted all experimental data available at that time according to method *B*(ii). The measurements of Simerska (1961) give consistent results irrespective of the method applied.

A survey of all results seems to indicate that all *B*(i) values lie lower than the *B*(ii) values.

For gold the results of the present work are in agreement with those of Owen & Williams (1947).

The present value of Θ_0 for platinum is about 55% higher than the one found by Alexopoulos & Euthymiou (1954). This difference cannot be ascribed to the large random errors of the latter work but appears to be due to recrystallization in the wire specimen used during the measurements. In fact, the experimental data of

Table 1. *Θ values according to different methods*

Method	Silver		Gold		Platinum		Lead	
	Θ_0(°K)	$\Delta\Theta/\Delta T$	Θ_0(°K)	$\Delta\Theta/\Delta T$	Θ_0(°K)	$\Delta\Theta/\Delta T$	Θ_0(°K)	$\Delta\Theta/\Delta T$
A	195 ± 5	~ +7 %	160 ± 6	~ +15 %	238 ± 6	−6 %	~106	~ −12 %
B(i)	206 ± 4	−2·5 %	176 ± 3	−2·5 %	238 ± 4	−1·5 %	82 ± 2	−2 %
B(ii)	212 ± 7	−6 %	180 ± 5	−2·5 %	233 ± 5	−1·5 %	85 ± 3	−4 %
B(iii)	225 ± 15	−8 %	175 ± 5	−2·5 %	248 ± 20	~ −3 %	85 ± 6	−4 %

Table 2. *Θ values from X-ray reflexions according to different authors*

Metal	Authors	Method	Θ_0(°K)	$\Delta\Theta/\Delta T$
Silver	Andriessen (corrected by Haworth)	*B*(i)	239	—
	Boskovits *et. al* (corrected)	*B*(i)	198	−2·5 %
	Spreadborough & Christian*	*B*(i)	191 ± 8	−2·5 %
	Haworth*	*B*(i)	197 ± 6	−2·5 %
	Herbstein	*B*(ii)	218	−6 %
	Simerska	*A*, *B*(i), *B*(ii)	209	−3 %
	Present work*	*B*(ii)	212 ± 7	−6 %
Gold	Owen & Williams	*B*(i)	175	−2·5 %
	Present work*	*B*(i), *B*(ii), *B*(iii)	177 ± 5	−2·5 %
Platinum	Alexopoulos & Euthymiou	—	156 ± 26	—
	Present work*	*B*(i), *B*(ii)	236 ± 5	−1·5 %
Lead	Chipman*	*B*(ii)	85 ± 4	−4 %
	Present work*	*B*(ii), *B*(iii)	85 ± 6	−4 %

* Corrected for T.D.S.

the above authors show a remarkable discontinuity at about 800 °K, a temperature which is near the recrystallization threshold of platinum.

In the case of lead the results of the present work are in complete agreement with those of Chipman (1960).

In conclusion, it can be stated that for gold and platinum the variation of Θ with temperature can be accounted for by the volume expansion. In the case of silver and lead this variation is larger than that corresponding to the volume expansion alone and is possibly due to the anharmonicity of the lattice vibrations. However, the errors of the X-ray measurements and the uncertainties inherent in the calculation of Θ do not allow a more detailed picture of the dependence of Θ on temperature. This holds especially at low temperatures.

APPENDIX

Equation (5) is obtained in the following way: By the use of Bragg's equation and the linear thermal expansion relation, the factor $\sin^2\theta/\sin^2\theta_0$ of equation (2) can be written to a first approximation:

$$\sin^2\theta/\sin^2\theta_0=1-2\bar{\alpha}(T-T_0) \qquad (6)$$

where $\bar{\alpha}$ is the mean thermal expansion coefficient in the region $T-T_0$. By inserting equations (6) and (4) into (2) and remembering that Ψ is close to unity for $T>\Theta$ we obtain:

$$R=\frac{T_0}{\Theta_0^2}-\frac{T(1+\mu T)}{\Theta_0^2(1+\mu T_0)}\,.\,\{1-2\bar{\alpha}(T-T_0)\}$$

and by rearranging,

$$R=\Theta_0^{-2}\,.\,(1+\mu T_0)^{-1}\,.\,(T_0-T+\tau_1)\,.\,\{1+\mu(T+T_0+\tau_2)\} \qquad (7)$$

where $\tau_1=2\bar{\alpha}T(T-T_0)$ and

$$\tau_2=\frac{2\bar{\alpha}T_0T}{1-2\bar{\alpha}T}\,.$$

Equation (7) is identical with equation (5).

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Die automatisierte Faltmolekülmethode

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A procedure which extends the use of the convolution molecule method of Hoppe to three-dimensional studies with the aid of a computer is described. Two examples of structure determination with this procedure are given.

Einleitung

Die Faltmolekülmethode (Hoppe, 1957*a*, *b*) beruht auf einer nach der Kristallsymmetrie geordneten Zerlegung der Pattersonsynthese in moleküleigene Funktionen. Diese Funktionen werden (bei zumindest teilweise bekannter Molekülstruktur) in der Pattersonsynthese aufgesucht, um so Orientierung und Translation der Moleküle zu bestimmen.

Die Kristallelektronendichtefunktion sei als Summe der molekularen Elektronendichten dargestellt:

$$\varrho(\mathbf{x})=\sum_k \varrho_k(\mathbf{x}-\mathbf{x}_k) \qquad (1)$$