possible double bond character of C_1C_2 is at most 0.05 ± 0.04.

The C_1C_2 and C_2C_2' bonds are between carbons in the sp^2 state of hybridization and are close to the expected values for pure single and double bonds of 1.48 and 1.337 Å (Cruickshank & Sparks, 1960).

The strain for the isolated anion would be completely relieved if the ion became non-planar with the carboxyl groups tilted by 46° about their C–C bonds so that O_1 and O_1' lay on opposite sides of the plane of the carbons at distances of 0.85 Å from the plane. The $C=C$ bond prevents the carbons becoming appreciably non-planar. Such a configuration would require a different structural arrangement and packing.

O_1 and O_2 have much larger temperature parameters in a direction perpendicular to the molecular plane, although C_1 and C_2 have not. These extra temperature factors suggest either a r.m.s. oscillation of the carboxyl groups of approximately 15° with a r.m.s. displacement for O_1 and O_1' of 0.3 Å out of the plane, or a random distribution throughout the structure of non-planar ions with O_1 either above or below the carbon plane by 0.3 Å. With O_1 and O_1' on opposite sides of the plane H_1 would still be in the plane so

that it would not have a larger temperature parameter perpendicular to the anion plane. This is exactly the result obtained, although the shape of the H_1 sections in Fig. 6 of the previous paper may not be very significant.

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The Temperature Dependence of the Debye Temperature Θ of Silver by X-ray Diffraction Measurements

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The study of the temperature dependence of the characteristic temperature Θ for silver in the temperature range from 18 to 760 °C. is presented. The determination of Θ-values from measured X-ray data was carried out by three procedures. Comparison with previous measurements is given.

1. Introduction

Several authors have presented experimental data of the temperature variation of the Debye characteristic temperature Θ of silver obtained by X-ray diffraction methods (Andriessen, 1935; Boskovits et al., 1958; Spreadborough & Christian, 1959a). Their results differ considerably so that the experimental redetermination of the dependence of Θ_{Ag} on T seems desirable. This work is a part of a detailed X-ray diffraction study of the atomic vibrations in Al–Ag equilibrium solid solutions.

2. Experimental technique

The finely grained powder of silver used for our diffraction measurements was prepared by the reduction of a 5% solution of silver nitrate (p.a.) in the

presence of ammonia with a dilute solution of formaldehyde. The sample was a compressed platelet ($10 \times 10 \times 2$ mm.) of this powder. A diffraction photograph showed the absence of any preferred orientation. The sample was annealed for 10 hr. at 650 °C. in vacuum before the measurements were carried out. A series of diffraction photographs was taken in a Unicam high-temperature vacuum camera in the temperature range 18 to 760 °C. A bent quartz crystal of the Johansson type was used for monochromatization of Cu $K\alpha$ radiation. The semifocusing method was applied, the inclination of the flat sample surface to the direct beam being 29° and the distance from the focus to the centre of the cylindrical camera of the diameter 190 mm. being 52 mm. In this way we have obtained the optimum resolution of the last eight diffraction lines (Simerská & Syneček, 1959). The

Θ-values were determined from the relative integrated intensities of all diffractions lines with the exception of 111 and 002.

3. Methods for determination of Θ-values

The variation of Θ with temperature was determined in three ways.

(A) Assuming the atomic scattering factor to be known with sufficient accuracy for an atom at rest we can use the following procedure. For the integrated intensities I_T divided by usual factors (Lorentz, polarization, absorption, multiplicity and in our case the square of the atomic scattering factor) we can write

$$\ln I_T = (AT/\Theta_T^2) \sin^2 \theta + \ln c_T . \qquad (1)$$

In this relation, which is obeyed for sufficiently high temperatures $T > \Theta$ (James, 1954), θ denotes the Bragg angle, $A = -12h^2/(mk\lambda^2)$ and c_T is a constant on the absolute intensity scale. The plot of $\ln I_T$ against $\sin^2 \theta$ is a straight line with slope

$$K = AT/\Theta_T^2 . \qquad (2)$$

This relation determines the Θ_T-value for a given temperature T.

(B) Measurements of the intensity decrease of a certain diffraction line with increasing temperature are made usually to eliminate the influence of inaccuracy of atomic scattering curve in the $\Theta(T)$-determination. It is then assumed either that Θ_T remains constant in a small temperature range or that Grüneisen's law is fulfilled so that the following relation holds for two temperatures T and T_1

$$\Theta_T/\Theta_{T_1} = (V_{T_1}/V_T)^\gamma. \qquad (3)$$

According to Paskin (1957) the Θ_{T_1}-value can be determined from the plot of logarithm of intensity ratio against the reduced temperature $T'=T(V_T/V_{T_1})^{2\gamma}$. These methods seem to us appropriate for counter technique if either of the assumptions is fulfilled with sufficient accuracy.

The following procedure can be recommended when the film technique is used and when the intensities of diffraction lines of each photograph are measured in different relative scales. The relation similar to (1) can be written for I'_T divided by usual factors except the atomic scattering factor f:

$$\ln I'_T = (AT/\Theta_T^2) \sin^2 \theta + \ln f^2 + \ln c_T . \qquad (4)$$

The difference of relation (4) for two different temperatures yields a straight line with slope

$$K_T = A[(T/\Theta_T^2) - (T_r/\Theta_{T_r}^2)] , \qquad (5)$$

where T_r is an arbitrary reference temperature.

(i) In such cases, when Grüneisen's law is valid, relation (5) can be rewritten using Paskin's expression for the reduced temperature T' (Paskin, 1957). We obtain

$$K_T = (A/\Theta_{T_r}^2)(T' - T_r) . \qquad (6)$$

The plot of K_T against T' gives a straight line from the slope of which Θ_{T_r} can be determined. Further values of Θ_T follow from relation (3) with $T_1 = T_r$.

(ii) As regards the approximative nature of assumptions about the relationship of Θ with T it seems useful to us to try the possibility of determining this relationship directly from (5). This would be possible if the average vibrational state of the lattice expressed by Θ were known at least for one temperature. Choosing this value as Θ_{T_r}, the other values of Θ_T could be then determined from (5). It should be mentioned that Θ-values obtained by various methods can differ not only due to different experimental errors but also due to the different averaging of the vibrational modes in deriving Θ (James, 1954; Blackman, 1955). The following procedure can be of some use if there is a rather large scatter of Θ_{T_r}-values. We choose several values of Θ_T from sufficiently large interval so as to contain the true X-ray value of Θ_{T_r}. Each value gives according to (5) one $\Theta(T)$-curve. A set of curves resulting in this way is plotted on the same graph together with the values of Θ_T determined by the procedure (A). If all of these Θ_T fit within the experimental errors on to one $\Theta(T)$-curve, then this curve can be supposed to represent the correct one. On the other hand the agreement of these two procedures can be seen as a proof of the correctness at least of the relative values of the atomic scattering curve used in (A).

4. Results of measurements

All three procedures were used for the determination of the temperature dependence of Θ. The maximum variation of temperature during the exposure was not greater than ± 2 °C. The temperature was controlled for each diffraction photograph by the measurement of the lattice parameter a using the method of ratios for cylindrical camera described by Černohorský (1959). The variation of a with T for silver was taken
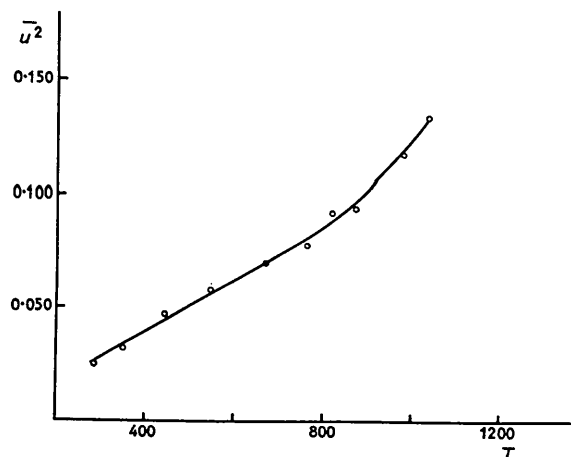

Fig. 1. The variation of $\overline{u^2}$ with T for silver.

from the measurements of Reynolds & Hume-Rothery (1938) and Spreadborough & Christian (1959b).

For the determination of Θ_T according to (A) the values of the atomic scattering factor of silver given by Sagel (1958) including the dispersion corrections were used. The results are given in Table 1. The variation of the total mean square displacements $\overline{u^2}$ with temperature is shown in Fig. 1. The $\overline{u_T^2}$-values were determined in the same way as Θ_T from (1) expressing the value of K by the relation

$$K = -(16\pi^2/3\lambda^2)\overline{u_T^2}.$$

Table 1. *The temperature dependence of Θ for silver according to* (A)

T (°K.)	Θ (°K.)	T (°K.)	Θ (°K.)
291	208	763	198
352	211	819	190
445	200	873	189
547	196	977	183
669	197	1033	176

Using the procedure described in (B)(i) the values of K_T were determined for all these temperatures choosing $T_r = 291$ °K. The results are given by points in Fig. 2 (solid line). The values of K_T were then plotted against the reduced temperature T'' using $\gamma = 2,4$. These points fall with sufficient accuracy on a straight line (dashed line in Fig. 2) except the last two. This can be explained as due to the increased anharmonicity of the lattice vibrations near the melting point. The same effect shows Fig. 1 for the last two values of $\overline{u^2}$. According to (6) the value of $\Theta_{T_r} = 209$ °K. was determined for $T_r = 291$ °K.
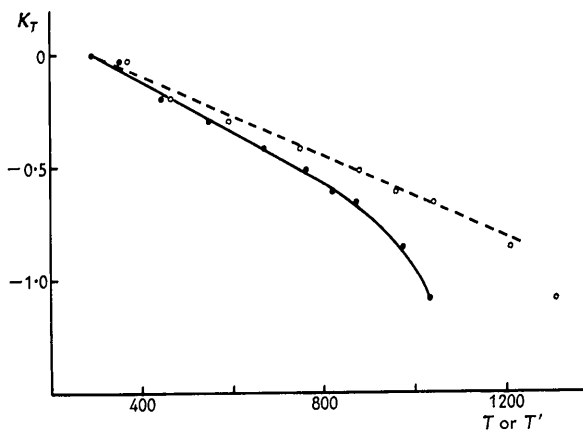

Fig. 2. The plot of K_T obtained from (5) versus T or T'.

For the application of procedure (B)(ii) the values of K_T, which are given by a solid curve in Fig. 2, were used. The Θ_T-values were then calculated from (5) choosing subsequently the values of Θ_{T_r} equal to 170, 190, 200, 210 and 230 °K. The resulting set of
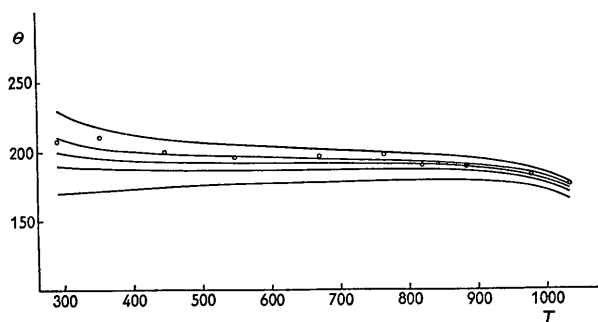
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Fig. 3. The illustration of procedure (B) (ii); the curves shown refer to $\Theta_{T_r} = 170$, 190, 200, 210 and 230 °K., the circles follow from procedure (A).

curves is represented in Fig. 3. The circles denote the values Θ_T obtained according to (A). Fig. 3 shows that the latter values can be fitted with sufficient accuracy to the curve calculated from (5) with $\Theta_{T_r} = 210$ °K. within the whole temperature range investigated. For this Θ_{T_r} the values of Θ_T corresponding to the temperatures of measurement are in Table 2.

Table 2. $\Theta(T)$-*dependence for silver according to* (B)(ii)

T (°K.)	Θ (°K.)	T (°K.)	Θ (°K.)
291	210	763	194
352	203	819	193
445	199	873	191
547	197	977	185
669	195	1033	175

5. Conclusion

The results of previous measurements of the temperature dependence of Θ mentioned in the introduction are revealed in Fig. 4. Paskin's method was used to convert the A-values taken from the Table II of Andriessen's paper into the appropriate Θ-T dependence. The results are given by the curve (a) in Fig. 4. The measurements of Boskovits et al. (1958) are given by crosses and their interpolated curve is
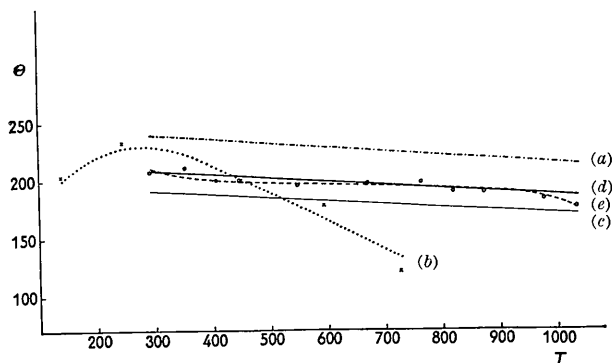

Fig. 4. The comparison of our results with the previous measurements: (a) Andriessen, (b) Boskovits et al., (c) Spreadborough & Christian; the circles and curves (d), (e) present author.

represented by the dotted line (b). The value $\Theta_{T_r} = 191$ °K. for $T_r = 293$ °K. as determined by Spreadborough & Christian (1959) gives according to relation (3) the temperature dependence of Θ indicated in Fig. 4 by a curve (c). It can be seen that the $\Theta(T)$-curves obtained from X-ray data by various authors differ considerably. For this reason three different procedures were used in our paper for deriving $\Theta(T)$-dependence from X-ray measurements. The resulting Θ_T-values obtained from our measurements applying (A) are given in Fig. 4 by circles, and in the same figure the $\Theta(T)$-curves resulting from (B)(i) and (B)(ii) are represented by the lines (d) and (e) respectively. Fig. 4 shows that all three procedures yield practically identical $\Theta(T)$-curves. The reliability of our measurements can be demonstrated especially by the agreement of the results obtained by assuming the knowledge of the scattering curve of the atom at rest in (A) and on the other hand by assuming the change of Θ with temperature according to Grüneisen's law in (B)(i), which is thus closely obeyed by silver up to the temperature of about 900 °K. The value of $\Theta_0 = 218$ °K. for $T = 0$ °K. obtained by extrapolation in the curve resulting from (B)(i) is also sufficiently close to the value of $\Theta_0 = 225 \cdot 3$ °K. deduced from specific-heat measurements (Corak, Garfunkel, Satterthwaite & Wexler, 1955).

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X-ray Studies of Molecular Overcrowding. II. The Crystal and Molecular Structure of o-Chlorobenzoic Acid

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o-Chlorobenzoic acid crystallizes in the monoclinic system, space group $C2/c$, with eight molecules in a unit cell of dimensions

$$a = 14 \cdot 73, \quad b = 3 \cdot 90, \quad c = 25 \cdot 50 \text{ Å}, \quad \beta = 112° \, 40'.$$

The crystal structure, which consists of centrosymmetrical hydrogen-bonded dimers, was elucidated initially in projection. The final atomic parameters were obtained from a least-squares treatment of the three-dimensional data, a total of 1034 observed structure factors being employed. The strain which would be imposed on a planar ideal molecule is relieved in a number of ways.

(i) The carboxyl group is rotated about the exocyclic C–C bond $13 \cdot 7°$ out of the plane of the benzene ring.

(ii) The chlorine atom and the exocyclic carbon atom are displaced $+0 \cdot 036$ and $-0 \cdot 058$ Å, respectively, out of the plane of the benzene ring.

(iii) The exocyclic C–C and C–Cl bonds are displaced sideways so that the normal valency angles of $120°$ are increased to $122 \cdot 5°$ and $124 \cdot 7°$, respectively.

1. Introduction

That steric interactions between adjacent non-bonded atoms may have an appreciable effect on molecular properties such as ultra-violet absorption has long been recognized and an extensive literature exists concerning both experimental and theoretical aspects of the subject. See, for example, Gray (1958).