References

ALLAVENA, M. (1965). *Cahiers Phys.* **19**, 401.

BARTELL, L. S. & GAVIN, R. M.(1964). *J. Amer. Chem. Soc.* **86**, 349.

BONHAM, R. A. (1965). *J. Chem. Phys.* **43**, 1103, 1460, 1933, 1434.

BONHAM, R. A. (1967). Private communication.

BONHAM, R. A. & COX, H. L. JR (1967). *J. Chem. Phys.* **47**, 3504.

CADE, P. E. & HUO, W. M. (1966*a*). *Techn. Report. Chicago University.*

CADE, P. E. & HUO, W. M. (1966*b*). *J. Chem. Phys.* **45**, 1063.

COOPER, M. J., ROUX, M., CORNILLE, M. & TSAPLINE, B. (1968). *Phil. Mag.* **18**, 309.

CORNILLE, M. (1967*a*). Thèse de Doctorat, Paris.

CORNILLE, M. (1967*b*). 12*th Sagamore Conference AMRA.* Syracuse Univ. Press.

DUMOND, J. W. M. (1933). *Rev. mod. Phys.* **5**, 1.

Intensities and Structure Factors Conference Report, (1969). *Acta Cryst.* A**25**, Part 1.

KILBY, G. E. (1965). *Proc. Phys. Soc.* **86**, 1037.

MOCCIA, R. (1964). *J. Chem. Phys.* **40**, 2164.

MOCCIA, R. (1967). *Theor. Chim. Acta (Berlin),* **8**, 8.

RANSIL, B. J. (1957). *Techn. Rep. Chicago Univ.* **9**.

ROUX, M., CORNILLE, M., TSAPLINE, B., ROUAULT, M. & TAVARD, C. (1967). *Acta Cryst.* **22**, 634.

SACHS, L. M. (1961). *Phys. Rev.* **24**, 1283.

TAVARD, C. (1966). *Cahiers Phys.* **195**, 397.

TAVARD, C. & ROUX, M. (1965). *C. R. Acad. Sci. Paris,* **260**, 4460, 4933.

Acta Cryst. (1970). A**26**, 108

The Temperature Dependence of Lattice Vibrations in Gold from X-ray Diffraction Measurements*

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The measurements of the Debye characteristic temperatures Θ and mean-square vibrational amplitudes $\overline{u^2}$ of gold in the temperature range from 300 to 1150°K are presented. All data were determined from the X-ray integrated intensities of a gold single crystal. The room temperature value $\Theta = 188 \pm 4$°K was found to be larger than Θ-values reported in the literature from X-ray data. The new value of Θ can be compared, however, with $\Theta = 186 \pm 8$°K calculated from the specific heat value of $\Theta_D = 178 \pm 8$°K and Poisson's ratio for gold. The temperature dependence of Θ is in satisfactory agreement with the volume dependence given by Grüneisen's law.

The Debye characteristic temperature was determined because of an apparent anomaly in the curve of thermal vibrational amplitudes *versus* concentration resulting from the X-ray diffraction measurements. If the room temperature value of $\Theta = 177 \pm 5$°K for gold reported by Alexopoulos, Boskovits, Mourikis & Roilos [*Acta Cryst.* (1965) **19**, 349] were employed a sharp drop of the $\overline{u^2}$ *versus* concentration curve would result for silver–gold alloys of high gold content. However, if the value of $\Theta = 188 \pm 4$°K reported in this investigation together with the value of $\Theta = 190 \pm 4$°K for an Ag–94·9 atom per cent Au are plotted on the above curve a smooth curve of $\overline{u^2}$ *versus* gold composition is obtained.

Introduction

This X-ray diffraction study of lattice vibrations in gold resulted as a consequence of a detailed investigation of thermal vibrations in silver–gold alloys (Simerska, Synecek & Chessin, 1969). The mean-square vibrational amplitudes, $\overline{u^2}$, of atoms in these alloys have been found by us to be lower as compared with their values in pure metallic components. The deviations of the $\overline{u^2}$ values from the mean of silver and gold data were much larger than the negative excess thermodynamic properties of silver–gold alloys (White, Orr & Hultgren, 1957) would indicate for vibrational contributions. The data for silver-rich solid solutions were consistent with previous X-ray diffraction measurements on pure silver (Herbstein, 1961; Simerska, 1961; Alexopoulos, Boskovits, Mourikis & Roilos, 1965). On the other hand, the mean-square vibrational amplitudes of gold extrapolated from the $\overline{u^2}$-curve for gold-rich solid solutions was not consistent with previous measurements of Θ reported by Owen & Williams (1947) and Alexopoulos *et al.* (1965). Their low value of Θ would lead to an abrupt break of the concentration dependence of $\overline{u^2}$ at high gold contents as well as to unusually high vibrational entropy changes, much higher in comparison with the excess entropies reported by White *et al.* (1957) for silver–gold alloys.

This paper presents the measurements of X-ray

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integrated intensities of a gold single crystal at room and elevated temperatures and their interpretation in terms of $\overline{u^2}$ and Θ.

Experimental

A single crystal of gold was used for X-ray diffraction intensity measurements in the temperature range from room temperature to 1150°K. Spectroscopic analysis of the gold used for growing the single crystals is given in Table 1.

Table 1. *Spectroscopic analysis of gold in parts per million*

Mg	less than 1
Pb	2
Si	less than 1
Cu	less than 1
Ag	less than 1

All other elements were not detected by standard spectrographic methods. The high-purity gold charge placed in a graphite crubible of 1 cm in diameter was melted in an atmosphere of pure argon. The melt was cooled 1°C per hour from 5°C above to 2°C below the melting point and then held at this temperature for three days. Laue diagrams taken from the polished and etched surface revealed the sample to be a single crystal.

The specimen with a flat surface, *i.e.* cross section of the ingot, was aligned with one of the $[1\bar{1}0]$ directions coincident with the ω axis of the X-ray diffractometer (Picker) provided with a high-temperature vacuum attachment (Electronics and Alloys). No efforts were made to cut the crystal along any orientation. The orientation of the free surface of the crystal was such that the $[1\bar{1}0]$ direction was within four degrees of lying in this surface but no Bragg plane measurable was in this surface. The $[1\bar{1}0]$ direction was brought into coincidence with the ω-axis after the crystal was mounted on the high temperature vacuum attachment by means of a suitable rotation about the χ-axis. A chromel–alumel thermocouple was fixed with high-temperature cement to the surface of the crystal just above the area used for X-ray diffraction. The crystal was heated for two hours at 1100°K before starting the measurements. The beam of molybdenum radiation was monochromatized by using the 333 reflection from a singly-bent silicon crystal adjusted to eliminate the $K\alpha_2$ component. The intensity data were collected using a scintillation detector and pulse-height discriminator.

Alignment of the crystal permitted us to measure the integrated intensities of planes belonging to the $[1\bar{1}0]$ zone. All planes accessible to the experimental arrangement were employed. The integrated intensities of the following reflections were recorded at room temperature: 115, 335, 226, 337, 446, 228, 448, 339, and 2, 2, 10. The temperature dependence of $\overline{u^2}$ and Θ was investigated from the intensity decrease of the 224 and 226 reflections in the range from room temperature to 1150°K in approximately 100°K steps. Automatic control and continuous monitoring held the temperature constant within ±2°C during the measurement. The ω-scanning mode, *i.e.* stationary-detector rotating-crystal method, was used for the measurement of integrated intensities. The total number of pulses was counted during a scanning range of 8° and the background was measured for two minutes at the 4° positions on both sides of the peak.

For comparison of our results on gold with those obtained for high-gold Ag–Au alloys, the results of the room temperature measurement for Ag–94·9 atomic per cent Au single crystal are presented here. The single crystal of this alloy was kindly supplied by Dr L. Slifkin of the University of North Carolina. All diffraction measurements were carried out in the same way as those for the gold crystal. Similarly the zonal planes of the $[1\bar{1}0]$ axis were used and the following reflections were recorded: 333, 335, 444, 553, 446, 555, 664, 557 and 666.

Evaluation of $\overline{u^2}$ and Θ

The mean-square displacements, $\overline{u^2}$, of atoms from their equilibrium positions were determined from the measured integrated intensities using the well-known relation valid for isotropic vibrations in simple cubic structures:

$$I(hkl) = cI_0(hkl) \exp\left(-\frac{16}{3}\pi^2\overline{u^2}\,\frac{\sin^2\theta}{\lambda^2}\right). \qquad (1)$$

Here $I(hkl)$ is the relative measured integrated intensity of the hkl reflection, c is the scale factor, θ is the Bragg angle and λ the wavelength of X radiation. The term $I_0(hkl)$ denotes the calculated integrated intensity in the absence of thermal vibrations and is given by the product of usual factors dependent on the θ value of the respective hkl reflection. These factors include the Lorentz factor corresponding to the single crystal measurements, the polarization factor for a crystal monochromated beam, f^2-values corrected for dispersion and the absorption factor.

Simple calculation gives for the angular dependent part of the absorption factor the following expression (Bragg, 1914)

$$A(\theta) = 1 - \frac{\tan\delta}{\tan\theta} \qquad (2)$$

where δ gives the angle between the reflecting plane and the surface of the crystal. The sign of δ is positive if the angle between the direct beam and the surface of the crystal in the reflecting position is larger than θ and *vice versa.*

The orientation of the surface of the crystal was such that $\delta = +14{\cdot}12°$ for the (335) plane and the corresponding value for the Ag–94·9 atom % Au single crystal reported here was $\delta = -4{\cdot}52°$ for the (335) plane. The reader may refer to James (1954, pp. 278–281) for clarification of this geometry. All reflection intensities were measured only if both the incident and diffracted beam angles made with the crystal surface exceeded 10° within the entire scanning interval. This precaution was taken to eliminate any excessively large absorption corrections and thus uncertainties due to this correction were minimized.

All measured integrated intensities $I(hkl)$ were corrected for one-phonon contribution to the thermal diffuse scattering. A simple correction for single-crystal data was derived and is presented in a separate paper (Synecek, Simerska & Chessin, 1969).

The following procedures were used for evaluation of the measured data.

(*A*) At room temperature all accessible reflections had favorable peak to background ratios so that the plot of $\ln[I(hkl)/I_0(hkl)]$ against $\sin^2\theta$ was used for the determination of $\overline{u^2}$ values. From relation (1) it follows that this plot yields a straight line with the slope

$$K = -\frac{16\pi^2}{3\lambda^2}\overline{u^2}. \quad (3)$$

The Debye characteristic temperature Θ can be determined from $\overline{u^2}$ using the well-known relation (James, 1954)

$$\overline{u^2} = \frac{9h^2T}{4\pi^2mk\Theta^2}\{\Phi(\chi)+\chi/4\}. \quad (4)$$

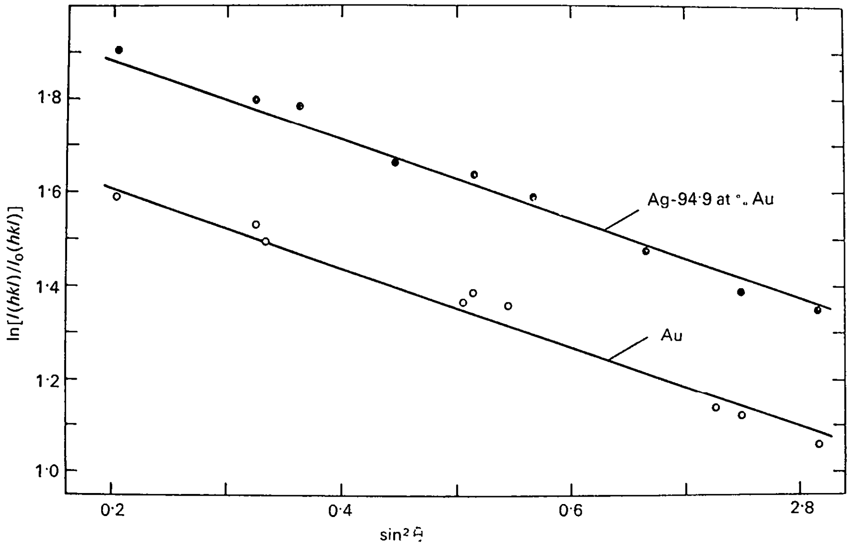

Fig. 1. Plot of $\ln\frac{I_r(hkl)}{I_0(hkl)}$ *versus* $\sin^2\theta$ at room temperature for gold and Ag–94·9 atom % Au.

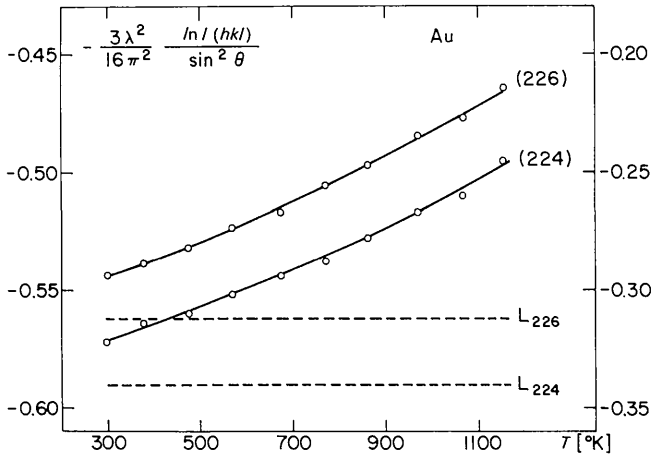

Fig. 2. The values of $-\frac{3\lambda^2}{16\pi^2}\frac{\ln I(hkl)}{\sin^2\theta}$ *versus* temperature for the 224 and 226 reflections of gold (the right-hand side scale corresponds to the 226 reflection).

The plots of ln $[I(hkl)/I_0(hkl)]$ against $\sin^2\theta$ gave at room temperature for gold the value $\overline{u^2}=0{\cdot}0188$ Å^2 and for the Ag–94·9 atomic per cent Au alloy $\overline{u^2}=0{\cdot}0187$ Å^2. The corresponding values of Θ are: $\Theta=188\pm4$°K for gold and $\Theta=190\pm4$°K for the Ag–94·9 atomic per cent Au alloy. Both plots of the data used for the above evaluations are given in Fig. 1.

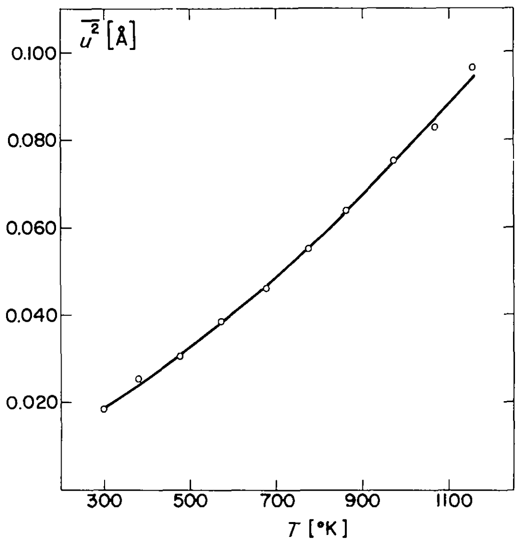

Fig. 3. The $\overline{u^2}(T)$ dependence of gold.

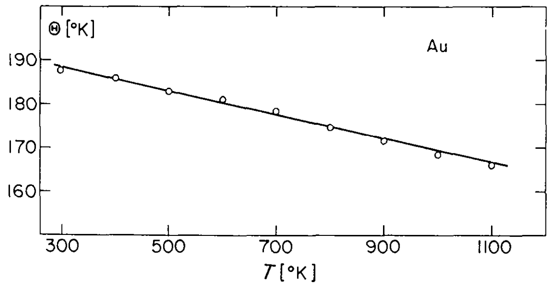

Fig. 4. The $\Theta(T)$ dependence of gold.

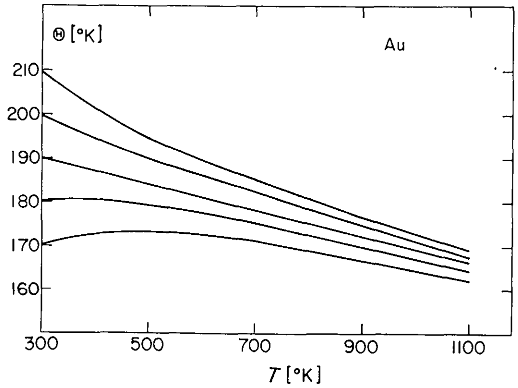

Fig. 5. Application of Chipman's method for constructing the plots of $\Theta(T)$ dependence for gold.

(B) The intensities of two lower angle reflections, 224 and 226 were used for the determination of the temperature dependence of $\overline{u^2}$. For the evaluation of $\overline{u^2}$ from the measured intensities relation (1) was rewritten in the following way

$$-\frac{3\lambda^2}{16\pi^2}\,\frac{\ln I(hkl)}{\sin^2\theta}=\overline{u^2}(T)+k$$

where

$$k=-\frac{3\lambda^2}{16\pi^2\sin^2\theta}\ln cI_0(hkl)\,. \qquad (5)$$

The plots of (5) calculated from measured intensities of both reflections are given in Fig. 2. The dependence of $\overline{u^2}$ *versus* temperature can be determined from each of these curves by finding the zero level, L. These levels L_{224} and L_{226} are indicated by broken lines and were found from the known value of $\overline{u^2}$ at the room temperature determined in (A). The $\overline{u^2}(T)$ dependence is shown in Fig. 3 and was constructed from both curves in Fig. 2. This $\overline{u^2}(T)$ curve was used for determining the Θ values from relation (4). The resulting $\Theta(T)$ dependence is shown in Fig. 4 and gives the value $\Theta=188$ °K for room temperature.

(C) Another approach to the solution of this problem was suggested by Chipman (1960). A family of Θ–T curves can be drawn, similar to those shown in Fig. 5, assuming different values of a reference Θ usually at room temperature. In order to choose the correct curve from this family of curves prior additional information is required such as the absolute value of the Θ at some temperature or the shape of the Θ *versus* T curve. To obtain the absolute value of Θ requires a measurement of the power in the primary beam by methods such as the high-angle scattering from lucite, but we have found large uncertainties in this method as did Chipman (1960). It should be noted that other methods of determining the absolute power of the primary beam have been reported (Batterman, Chipman & De Marco, 1961) and we have recently verified that these methods provide excellent internal consistency (Kashiwase & Chessin, 1969). Additionally, there are significant enough uncertainties in other quantities such as the atomic scattering factors, the dispersion corrections and Compton scattering as to render theoretical calculations in doubt.

A second method that would help to determine the correct value of Θ would depend on information on the temperature dependence of Θ and hence would explicitly yield a Θ *versus* T curve. Unfortunately there is at present no theory which is capable of predicting the Θ *versus* T curve either with regard to magnitude or shape. The only recourse left open is that implicit in the method described by Chipman of choosing the most reasonable Θ–T curve and comparing these results with the determinations made above. This procedure was applied to our measured temperature dependence of integrated intensities of the 224 and 226 reflections and the trial values of Θ for room temperature were: 170, 180, 190, 200 and 210°K. The results are indicated in Fig. 5, where the mean values for the 224 and 226 reflections are given. In the absence of any other information the value of Θ was chosen so as to give the least temperature dependence of the family of curves shown in Fig. 5. This Figure shows that a reasonable trial value of Θ is 190°K. This is in good agreement with results obtained in § (*A*) and (*B*).

The Grüneisen's constant γ can be determined from X-ray diffraction and thermal expansion data. Grüneisen's law gives $\gamma = -(\mathrm{d} \log \Theta / \mathrm{d} \log V)$. The plot of $\log \Theta$ against $\log V$ should therefore be a straight line with a slope equal to $-\gamma$. For the construction of this plot we used our measured $\Theta(T)$ dependence obtained in (*B*) and the thermal expansion data for gold measured by Simmons & Balluffi (1962). This plot is shown in Fig. 6 and gives the value of $\gamma = 3{\cdot}06$.

Suitable precautions were taken with regard to the possibility of extinction effects. We assume that primary extinction is negligible because of the large mosaic distribution (*circa* 0·5° half-breadth). Secondary extinction does not appear to be a significant effect, based on the methods of Chandrasekhar (1960). Thus for the strongest reflection (333) and for the standard deviation $\eta = 2{\cdot}2 \times 10^{-3}$ radians and $g = 1{\cdot}3 \times 10^2$, the ratio of the integrated intensity with and without extinction is $\varrho/\varrho' = 1{\cdot}02$. g is called the secondary extinction coefficient.

The problem of multiple diffraction is a much more formidable one and may be conveniently discussed in two parts: determining all the possible reciprocal lattice points close enough to the Ewald sphere from which simultaneous reflections can occur, and determining the intensity effect in a given primary diffraction beam due to one or more secondary reflections. The geometric aspect of the problem was first solved graphically for all orientations of the crystal chosen for this investigation. A refinement was then carried out by computer calculations to determine precisely the rotations, $\pm\omega$, and the change in the reciprocal lattice vector from the origin of reciprocal space required to bring the suspected reciprocal lattice point onto the Ewald sphere corresponding to the incident beam and the primary diffracted beam geometry. The effect of these additional lattice points being on the sphere of reflection is either to extract energy from the primary diffracted beam (aufhellung) or to add energy to the primary diffracted beam *via* the secondary diffracted beams (umweganregung).

Adopting the formulation of Zachariasen (1965) and using a value of T for a reflected primary beam from an infinitely thick crystal it becomes clear that aufhellung is the dominant effect when a strong reflection is recorded. On the other hand a weak reflection can be strengthened if multiple reflection can take place when a reciprocal lattice point of a strong reflection is on the incident beam sphere. Only in one case was the latter true for our studies. This case consisted of the 002, the 226 and 224 being on the reflection sphere or close to it during the scan through the 664 reflection. However, a rotation about the diffraction vector of the 664 through 360° revealed that the total umweganregung was a maximum of 4% of the primary diffracted beam and that most likely the orientation of our gold crystal was not well enough aligned to produce any significant effects. The three goniometer angles could be aligned with no greater precision than 0·25°. The φ-motion of the high-temperature diffractometer could be set with a precision of $\pm 1°$ and most likely accounts for the absence of any multiple-diffraction effects. These observations were confirmed by calculating the effect of mis-setting the φ-angle by 1° on all reciprocal lattice points close to the Ewald sphere.

It was not possible to make azimuthal scans on more than two orientations, the 664 and 333 reflections, since the crystal face had to be cut parallel to these planes. These two cuts consumed the entire single crystal of gold. However, the significance of multiple diffraction effects on these experiments can be gained from an examination of the data. A plot of the raw data of $\ln (I_T/I_0)$ against $\sin^2 \theta$ for gold and for Ag–94·9 atom % Au shown in Fig. 1 further confirms that extinction and multiple diffraction did not introduce appreciable errors in the data.

Discussion of results

All different procedures described above gave for gold at room temperature the same value $\Theta = 188 \pm 4$°K. This value and the corresponding mean value of $\overline{u^2} = 0{\cdot}0188$ Å^2 fits well into our data on lattice vibrations in silver–gold alloys (Simerska, Synecek & Chessin, 1969). The comparison with the Ag–94·9 atomic per cent Au alloy was given in this paper; the corresponding data for this alloy are $\Theta = 190 \pm 4$°K and $\overline{u^2} = 0{\cdot}0187$ Å^2. The Θ-values indicated in the literature for gold from previous X-ray measurements are: $\Theta = 175$°K (Owen & Williams, 1947) and $\Theta = 177 \pm 5$°K (Alexopoulos *et al.*, 1965). The large difference between the latter values of Θ for gold and the value of Θ for the Ag–94·9 at % Au alloy would result in large

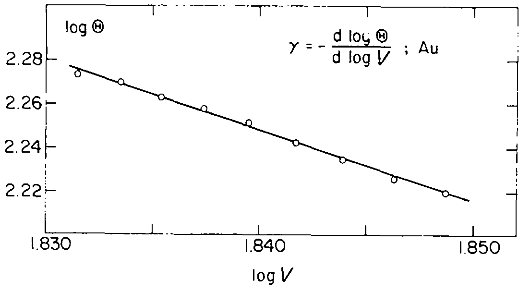

Fig. 6. The dependence of $\log \Theta$ on $\log V$ for the determination of Grüneisen's constant, γ.

vibrational entropy contributions on solid solution formation for alloys with high gold contents. White *et al.* (1957) found almost zero excess entropy of mixing for such alloys at the high gold concentration. This finding by these workers is in agreement with our value of Θ of gold which is almost identical with that of the Ag–94·9 at % Au alloy.

Our value Θ for gold can be compared with the value $\Theta_D = 178 \pm 8\,^\circ\mathrm{K}$ from specific heat measurements reported for room temperature in the review article by Gschneidner (1964). Because the transverse and longitudinal modes of vibration are averaged differently in X-ray and specific heat measurements, Θ_D should be multiplied by a factor dependent on Poisson's ratio, σ, to get the expected value Θ_M for diffraction measurements. The σ-value for gold is $\sigma = 0{\cdot}425 \pm 0{\cdot}010$ (Gschneidner, 1964) which gives $\Theta_M/\Theta_D = 1{\cdot}045$ (James, 1954). The corresponding Θ_M value is then $\Theta_M = 186 \pm 8\,^\circ\mathrm{K}$ which is in good agreement with our measurements.

Our results of the temperature dependence of Θ were compared with the volume dependence of Θ given by Grüneisen's law. The Grüneisen's constant $\gamma = 3{\cdot}06$ determined from our $\Theta(T)$-curve is in excellent agreement with $\gamma = 3{\cdot}04$ (Grüneisen, 1926) and $\gamma = 3{\cdot}09$ (Gschneidner, 1964) evaluated from specific heat measurements. An interesting aspect of this study is the observation that gold appears to have an X-ray Debye temperature, Θ_M, larger than the elastic-constant Debye temperature Θ_{El}. Of all the elements studied by both techniques gold appears to be the only one for which this statement is true. This observation has been made as a consequence of the deviation of the true vibrational spectrum from the parabolic form assumed by Debye theory. It has been variously argued on phenomenological grounds that Θ_{El} should be greater than Θ_M measured by X-ray diffraction. The measurements of elastic constants excite only the very lowest lattice frequencies while the real spectrum rises above that of the parabolic form. Thus the parabola that fits the true spectrum best over a significant portion of the frequency spectrum will be steeper than the parabola chosen for the lowest frequency values excited by elastic constant measurements. In the case of gold this phenomenological relationship appears to be reversed.

However, it is by no means clear that any correlation can be made at present because of the unsatisfactory state of the theory. At 0 °K almost all the methods of calculating the characteristic temperature, Θ_{El}, yield values for gold from 160 to 165 °K (see for example, Alers, 1965 and James, 1954) but there is no satisfactory theory that will allow us to calculate the characteristic Θ at elevated temperatures although De Launay (1956) discusses the behavior of Θ temperature dependence in the region where it first departs from Θ_0. An approach due to Post (1953) which hybridizes the methods of Debye and Born–von Karmin yields a calculated room temperature value of $\Theta_{El} = 170\,^\circ\mathrm{K}$ rising above that at 0 °K, which is in agreement with the significant increase of the specific heat Θ from measurements made from 0 to 30 °K (Martin, 1966). It appears, therefore, in the absence of a satisfactory theory that the only safe ground on which to correlate the different determinations of Θ is at, or very close ($\sim\Theta/50$ or $\Theta/100$), to 0 °K.

References

ALERS, G. A. (1965). *Physical Acoustics*, III B, 1. New York: Academic Press.

ALEXOPOULOS, K., BOSKOVITS, J., MOURIKIS, S. & ROILOS, M. (1965). *Acta Cryst.* **19**, 349.

BATTERMAN, B. W., CHIPMAN, R. D. & DE MARCO, J. J. (1961). *Phys. Rev.* **122**, 68.

BRAGG, W. H. (1914). *Phil. Mag.* **27**, 881.

CHANDRASEKHAR, S. (1960). *Advan. Phys.* **9**, 363.

CHIPMAN, R. D. (1960). *J. Appl. Phys.* **31**, 2012.

DE LAUNAY, J. (1956). *Solid State Physics*, **2**, 220. New York: Academic Press.

GRÜNEISEN, E. (1926). *Handbuch der Physik*, **10**. Berlin: Springer.

GSCHNEIDNER, K. A. JR (1964). *Solid State Physics*, **16**, 275. New York, London: Academic Press.

HERBSTEIN, F. H. (1961). *Phil. Mag. Suppl.* **10**, 313.

JAMES, R. W. (1954). *The Optical Principles of the Diffraction of X-rays*. London: Bell.

KASHIWASE, Y. & CHESSIN, H. (1969). To be published.

MARTIN, D. C. (1966). *Phys. Rev.* **141**, 576.

OWEN, A. E. & WILLIAMS, W. R. (1947). *Proc. Roy. Soc.* A**188**, 509.

PASKIN, A. (1957). *Acta Cryst.* **10**, 667.

POST, E. J. (1953). *Can. J. Phys.* **31**, 112.

SIMERSKA, M. (1961). *Acta Cryst.* **14**, 1259.

SIMERSKA, M., SYNECEK, V. & CHESSIN, H. (1969). To be published.

SIMMONS, R. O. & BALLUFFI, R. W. (1962). *Phys. Rev.* **125**, 862.

SYNECEK, V., SIMERSKA, M. & CHESSIN, H. (1969). To be published.

WHITE, J. L., ORR, R. L. & HULTGREN, R. (1957). *Acta Met.* **5**, 747.

ZACHARIASEN, W. H. (1965). *Acta Cryst.* **18**, 705.