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# The Characteristic Temperature of Silver from X-ray Reflections*

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The integrated intensity of diffraction lines (111) and (422) from a silver wire was measured at 6 different temperatures between 81 °K. and 774 °K. which were determined from the angular shift of diffraction line (422). By applying the formula of the usual Debye theory to each neighbouring pair of temperatures a value of $\Theta$ was obtained for the middle of the temperature interval. The following results were obtained, with an error in $\Theta$ of 3°–20°:

| Temperature °K. | 138 | 243 | 405 | 592 | 726 |
|---|---|---|---|---|---|
| Characteristic temperature | 203 | 233 | 200 | 178 | 121 |

The results, showing a decrease of $\Theta$ with increasing temperature, do not coincide with those of Andriessen. His measurements gave a constant value of $\Theta = 218$ up to 670 °K. Neither extinction nor oxidation can account for the low $\Theta$-values found from the present measurements.

## Introduction

The heat vibrations in solids can be investigated from the loss of intensity of the X-ray diffraction lines upon heating. By measuring the intensity at different temperatures the characteristic temperature $\Theta$ is obtained. Such measurements have been carried out in the past on a number of elements. The resulting values of $\Theta$ do not coincide with those obtained from measurements of specific heat, so that an investigation of a larger number of elements was advisable.

The present paper describes measurements on silver.

## Theoretical part

The temperature dependence of the intensity of X-ray powder reflections is given by the formula

$$P = P_0 \exp(-2M)\,, \tag{1}$$

where $P$ and $P_0$ are the integrated intensities of a line diffracted at temperature $T$ respectively in absence of any oscillation of the atoms.

The exponent $2M$ is given by:

$$2M = \frac{12h^2}{mk\Theta} \cdot \frac{\sin^2\theta}{\lambda^2}\left[\frac{\Phi(x)}{x}+\frac{1}{4}\right],$$

where

$$x = \frac{\Theta}{T}, \quad \Phi(x) = \frac{1}{x}\int_0^x \frac{\xi d\xi}{e^\xi - 1}$$

and $m$ the mass of the atom. The other symbols have the usual meaning. Formula (1) can also be written:

$$\ln P = \ln P_0 - \frac{12h^2}{mk\Theta} \cdot \frac{\sin^2\theta}{\lambda^2}\left[\frac{\Phi(x)}{x}+\frac{1}{4}\right] \tag{2}$$

From this we can calculate the ratio of the intensities $P_1$ and $P_2$ of a given diffraction line at two temperatures $T_1$ and $T_2$. We obtain:

$$\ln\frac{P_1}{P_2} = \frac{12h^2}{mk\Theta} \cdot \frac{\sin^2\theta}{\lambda^2}\left[\frac{\Phi(x_2)}{x_2} - \frac{\Phi(x_1)}{x_1}\right]. \tag{3}$$

Hence by measuring the intensities of a given diffraction line at two temperatures we can directly find $\Theta$.

In the light of the modern theory of heat vibrations $\Theta$ is not a constant but shows a slow change with temperature. In order to measure $\Theta$ for a given temperature, the intensity must be measured at two temperatures sufficiently near to each other so that $\Theta$ can be considered to remain constant in the temperature interval considered. On the other hand the temperature interval must not be choosen too small otherwise the method becomes inaccurate. Thus by measuring $P$ at a number of temperatures and applying formula (3) to each consecutive pair of measurements the change of $\Theta$ with temperature can be determined. As fluctuations of the primary intensity and of the efficiency of the counting apparatus could not be avoided, it was safer to measure the intensities of two diffraction lines at each temperature and use their ratio. If we call this ratio $P_{\text{rel}}$ formula (2) can be written:

$$\ln P_{\text{rel}} = \ln\frac{P_0}{P_0'} - \frac{12h^2}{mk\Theta} \cdot \frac{\sin^2\theta - \sin^2\theta'}{\lambda^2}\left[\frac{\Phi(x)}{x}+\frac{1}{4}\right], \tag{4}$$

where the unprimed and primed symbols designate each of the two diffraction lines. Applying formula (4) at two temperatures $T_1$ and $T_2$ which are sufficiently close to neglect the changes of the diffraction angles, we obtain:

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$$\ln \frac{P_{\mathrm{rel}_{T_1}}}{P_{\mathrm{rel}_{T_2}}} = \frac{12h^2}{mk\Theta} \cdot \frac{\sin^2\theta - \sin^2\theta'}{\lambda^2} \left[ \frac{\Phi(x_2)}{x_2} - \frac{\Phi(x_1)}{x_1} \right]. \qquad (5)$$

## Experiments and conclusions

The experiments were carried out with filtered copper radiation (32 pkV., 10 mA.). The X-ray tube with the necessary system of slits was fixed to an accurate goniometer. The scattering sample was a silver wire of 0·8 mm. diameter. Before use it was tested on a standard Debye–Scherrer camera in order to check that it was sufficiently microcrystalline and that it had no fibre texture due to drawing. A Geiger counter with an appropriate system of slits was fixed to the turning arm of the goniometer. The measurements were carried out on the diffraction lines (422) and (111). The intensity was measured point by point every 15 resp. 5 minutes of arc. The results were plotted and planimetered and the resulting areas were used as a measure of the corresponding integrated intensities $P$. The scattering sample was heated above room temperature by blowing a vertical stream of hot air onto the wire. For cooling below room temperature the wire was fixed to the bottom of a vacuum cryostat.

The temperature of each measurement was determined from the angular shift of line (422) by using formula

$$l_t = l_o[1 + 18{\cdot}72 \times 10^{-6}t + 7{\cdot}393 \times 10^{-9}t^2 + 7{\cdot}381 \times 10^{-12}t^3]$$

in the region of high temperatures, and formula:

$$l_t = l_o[1 + (17{\cdot}79066t + 0{\cdot}0034641t^2 + 0{\cdot}0_4 59343t^3 + 0{\cdot}0_6 35754t^4) . 10^{-6}]^*$$

in the region of low temperatures (temperature $t$ in °C.).

Under the experimental conditions line (422) had a half width of approx. 1·5 degrees of arc and the position of each peak could be determined with an accuracy of about 3 to 4 minutes of arc. Thus the error in temperature of each high temperature measurement, amounts to about 10°. In the low temperature measurements the cryostat had the same temperature at every run. Therefore the mean value of all the runs could be taken.

Table 1(*a*). *Low temperature measurements of intensities*

| 1st Run | | | 2nd Run | | | 3rd Run | | |
|---|---|---|---|---|---|---|---|---|
| $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ | $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ | $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ |
| 292 | 905 | 550 | 289 | 983 | 558 | 289 | 978 | 572 |
| 195 | 1112 | 571 | 195 | 1082 | 567 | 195 | 1055 | 546 |
| 81 | 1365 | 578 | 81 | 1322 | 575 | 81 | 1295 | 566 |

| 4th Run | | | 5th Run | | | 6th Run | | |
|---|---|---|---|---|---|---|---|---|
| $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ | $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ | $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ |
| 291 | 907 | 545 | 292 | 896 | 550 | 292 | 988 | 546 |
| 195 | 1074 | 554 | 195 | 1119 | 584 | 195 | 1143 | 592 |
| 81 | 1261 | 553 | 81 | 1366 | 605 | 81 | 1350 | 592 |

Table 1(*b*). *High temperature measurements of intensities*

| 1st Run | | | 2nd Run | | |
|---|---|---|---|---|---|
| $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ | $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ |
| 304 | 624 | 344 | 305 | 710 | 400 |
| 496 | 387 | 300 | 505 | 431 | 360 |
| 678 | 232 | 284 | 685 | 301 | 325 |
| 770 | 158 | 289 | 772 | 167 | 303 |

| 3rd Run | | | 4th Run | | |
|---|---|---|---|---|---|
| $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ | $T_{ok}$ | $P_{(422)}$ | $P_{(111)}$ |
| 304 | 631 | 348 | 304 | 626 | 360 |
| 518 | 419 | 329 | 511 | 444 | 339 |
| 678 | 284 | 307 | 671 | 256 | 322 |
| 777 | 142 | 255 | 778 | 158 | 289 |

In Tables 1(*a*) and (*b*) the experimental data for six independent runs at low temperature and four independent runs a high temperature respectively are listed. $\Theta$ for each temperature interval can now be obtained from formula (5), by using the data of each consecutive pair of temperatures. The results are given in Table 2 separately for every temperature interval and every run. The mean values of $\Theta$ have been plotted in Fig. 1 (full points) against the temperature of the center of the interval. The vertical lines indicate the mean error. The full curve gives the general trend of the results. The errors do not allow the determination of the form of the left part of the curve e.g. if it is horizontal or goes through a maximum at normal temperatures. On the other hand the decrease of $\Theta$ with increasing temperature is definite.

For reasons of comparison the values of $\Theta$ found by other investigators are shown in the same figure. The individual points give the values found from specific heat measurements (Meads, Forsythe & Giauque (1941) and Eucken, Clusius & Woitinek (1931)). This method is good for temperatures lower than $\Theta$ and hence reliable $\Theta$ values can be obtained only up to about 200 °K. The only determination of $\Theta$ at higher temperatures is due to Andriessen (1935). His method was similar to the one described in the present paper. The X-rays were diffracted on a powder of silver particles adhering to a quartz fibre. The particles had dimensions between 4 and 8 $\mu$, thus practically elimi-

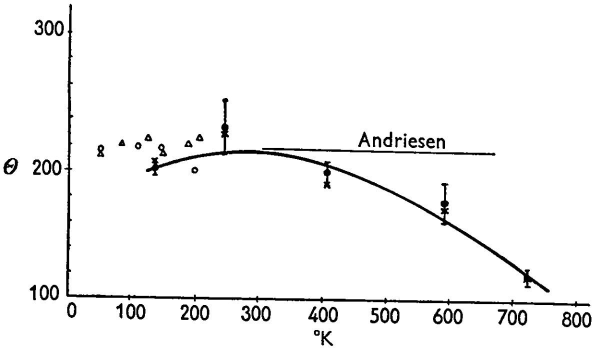

Fig. 1. Characteristic temperature of silver versus Kelvin temperature. ○ Meads–Forsythe–Giauque. △ Eucken–Clusius–Woitinek. ● and × present work.

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* Landolt–Börnstein. *Phys.-Chem. Tabellen*. 5th ed. Eg IIb and IIIc. § 247a.

Table 2. *The characteristic temperature of silver from X-ray reflections*

| Temperature interval | Run | $T_1$ | $T_2$ | Centre of temp. interval | $P_{\mathrm{rel}_{T_1}}$ | $P_{\mathrm{rel}_{T_2}}$ | $\log P_{\mathrm{rel}_{T_1}}/P_{\mathrm{rel}_{T_2}}$ | $\Theta$ | Mean value of $\Theta$ |
|---|---|---|---|---|---|---|---|---|---|
| 1st | 1 | 81 °K. | 195 °K. | 138 | 2·361 | 1·947 | 0·0839 | 193 | 203·2 ± 2·8 |
| | 2 | 81 | 195 | | 2·299 | 1·908 | 0·0810 | 196 | |
| | 3 | 81 | 195 | | 2·288 | 1·932 | 0·0733 | 205·5 | |
| | 4 | 81 | 195 | | 2·280 | 1·939 | 0·0704 | 209·5 | |
| | 5 | 81 | 195 | | 2·258 | 1·916 | 0·0712 | 208 | |
| | 6 | 81 | 195 | | 2·280 | 1·931 | 0·0723 | 207 | |
| 2nd | 1 | 195 | 292 | 243 | 1·947 | 1·645 | 0·0731 | 193 | 233·2 ± 19·6 |
| | 2 | 195 | 289 | | 1·908 | 1·762 | 0·0346 | 274 | |
| | 3 | 195 | 289 | | 1·932 | 1·710 | 0·0531 | 223 | |
| | 4 | 195 | 291 | | 1·939 | 1·664 | 0·0663 | 202 | |
| | 5 | 195 | 292 | | 1·916 | 1·629 | 0·0704 | 197 | |
| | 6 | 195 | 292 | | 1·931 | 1·810 | 0·0282 | 310 | |
| 3rd | 1 | 304 | 496 | 405 | 1·814 | 1·290 | 0·1480 | 194·5 | 200.4 ± 7·7 |
| | 2 | 305 | 505 | | 1·775 | 1·197 | 0·1711 | 184·5 | |
| | 3 | 304 | 518 | | 1·813 | 1·273 | 0·1536 | 201·5 | |
| | 4 | 304 | 511 | | 1·739 | 1·310 | 0·1230 | 221 | |
| 4th | 1 | 496 | 678 | 592 | 1·290 | 0·817 | 0·1984 | 163·5 | 177·5 ± 15·1 |
| | 2 | 505 | 685 | | 1·197 | 0·926 | 0·1115 | 217 | |
| | 3 | 518 | 678 | | 1·273 | 0·925 | 0·1387 | 183 | |
| | 4 | 511 | 671 | | 1·310 | 0·795 | 0·2169 | 146·5 | |
| 5th | 1 | 678 | 770 | 726 | 0·817 | 0·546 | 0·1750 | 124 | 120·6 ± 6·9 |
| | 2 | 685 | 772 | | 0·926 | 0·551 | 0·2254 | 106 | |
| | 3 | 678 | 777 | | 0·925 | 0·557 | 0·2202 | 114·5 | |
| | 4 | 671 | 778 | | 0·795 | 0·546 | 0·1632 | 138 | |

nating effects due to extinction. The intensity of the diffracted rays was determined from the blackening of a photographic film. The results which were obtained from several diffraction lines, gave a constant value of $\Theta = 218$ °K. from room temperature up to 400 °C. From that temperature on, it showed a gradual decrease.

Andriessen's results differ considerably from our own. We will attempt to discuss the possible reasons. An important source of errors in X-ray diffraction investigations is the change of extinction effects that occurs when the crystallites change either their dimensions or their degree of perfection. The present measurements were carried out in four consecutive runs during which the same scattering sample was repeatedly heated to 500 °C. and cooled. This treatment might change the extinction effects. As the diffraction lines (111) and (422) would not be influenced by such effects to the same degree their ratio would change. Another source of error might be the oxidation of the surface of the scattering material. As silver is opaque to X-rays, the diffraction occurs mainly on the surface of the wire. It is evident that the diffracted rays of line (422) have a shorter path in the oxide layer than line (111) and thus the intensities will not be diminished to the same extent.

However, the effects described above could not have influenced the present results. If the effects (change of extinction and oxidation) occurred gradually during the course of the measurements, the ratio for the two lines (when measured at the same temperature) would have changed gradually. No such change was found. If, alternatively, the effects occurred during the preliminary heatings, the ratio of the two lines would not have changed subsequently and thus no error in $\Theta$ would be introduced.

As no explanation could be found for the difference between the present results and those published by Andriessen, we decided to work out our data exactly in the same way as Andriessen did, in order to see if a different trend in $\Theta$ would appear. Instead of using formula (5) which contains the intensities of two diffraction lines, we applied the data of the high index line (422) to the formula (3). This method might have larger errors, produced by changes in intensity of the primary X-ray beam and by changes of efficiency in the counter, but the influence of extinction would be smaller. The results are given in Table 3.

Table 3. *Center of temperature interval* (°K.) *and characteristic temperature* ($\Theta$)

| °K. | 138 | 243 | 405 | 592 | 726 |
|---|---|---|---|---|---|
| $\Theta$ | 207 | 227 | 191·5 | 172·1 | 119·2 |

The results are shown in Fig. 1 in the form of crosses. We see that the general form of the curve remains unchanged.

## References

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