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DISCUSSION

JENNINGS: Have you measured the integrated intensities in Bragg reflexion with a view to obtaining the absolute value of the structure factor?

BROGREN: No. The measurements we are making actually allow a much more sensitive test of various theoretical wave functions than do measurements of the integrated Bragg intensities.

Our measurements were made to determine only the anomalous contribution to the atomic scattering factor. The accuracy demands in our experiments are higher than in experiments where only $|F|$ is sought and where F is not being divided into real and imaginary parts. However, the structure factor values could be derived from our experiments.

JENNINGS: There is at present disagreement to the extent of about 2% as to the integrated Bragg intensity of Ge 111. If you are in a position to make such a measurement easily, it would be most helpful if you could either publish such results or communicate them directly to those who have been active in making such measurements.

Acta Cryst. (1969). A**25**, 116

D2·1

Debye–Waller Factor and Anomalous Absorption (Ge; 293-5°K)

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PRESENTED BY G. BORRMANN

Experiments measuring the intensity of three reflexions from a 'very thick' Ge crystal (Laue case) were made, while the temperature of the crystal was lowered from 293 to 5°K. The variation of the intensity agreed with the dynamic theory, when the Debye temperature Θ, used for the evaluation of the Debye–Waller factor, was assumed to be 290°K throughout the temperature range. This result may suffer some slight correction in the future, but there is no variation of Θ at 20°K. Θ = constant contrasts with the specific heat data of Θ but essentially agrees with Batterman & Chipman's prediction.

The absorption of Ewald waves

The intensity of interfering X-rays transmitted through a 'thick' perfect crystal varies very much with the temperature of the crystal. This is mainly due to the imaginary part of the scattering factor, so it is a matter of absorption. All the wave fields produced under the condition of Bragg's law, each of them represented by a point (the tiepoint) on the dispersion surface, exhibit different absorption.* The one whose absorption is the weakest we call the least absorbable Ewald wave. Its two components ('two beam case') have equal intensities, its Poynting vector is parallel to the 'reflecting' lattice plane, and its nodal planes coincide with the reflecting lattice planes (in the case of a simple lattice, and, for instance, in the case of the even-numbered planes of the diamond lattice). At the exit surface of a thick crystal, whose reflecting net plane is perpendicular to the surface, the least absorbed Ewald wave will predominate. It will be decomposed, and one of the two beams or both may be measured. For some purposes it is a good approximation to neglect all the strongly absorbed wave fields. An example is our topic. For the final evaluation the well-known formulae of the integrated intensity in both directions were used.

The probability of the photoeffect, the main contribution to the absorption, would be zero, if all the electrons were concentrated in the nodes of the electric field. The thermal vibrations of the atoms and the finite volume of their electron cloud prevent the absorption from disappearing. The dynamic theory accounts for these two facts by introducing the factors D_h and W_h

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* At the Cambridge Meeting the name Ewald wave was proposed for such a wave field (see Ewald, 1917).

(W_h is sometimes called ε_0), both < 1. The absorption coefficient of the least absorbable Ewald wave becomes

$$\mu_{\min} = \mu(1 - D_h W_h)/\cos\theta\,, \tag{1}$$

where μ is the normal absorption coefficient, θ the Bragg angle; $\mu_{\min}$ is valid in the direction of the energy flow, *i.e.* parallel to the reflecting net plane.

D_h turns out to be the well known Debye–Waller factor. At $T \to 0\,°\text{K}$, D_h approaches the value 1, but cannot reach it because of the zero point energy. W_h is a matter of the wave mechanical theory of the photoeffect (Hönl), as was shown by Wagenfeld (1966). The result may be interpreted in the following way: the electrons behave as if they were concentrated very near to the nucleus. In our examples, W_h is $> 0{\cdot}99$; it can be omitted in our approximation because it does not seriously affect the temperature dependence of the intensity.

Using (1) one gets the ratio of the intensity I at the temperatures T_1 and T_2 of either component of the least absorbed Ewald wave:

$$I_1/I_2 = \exp\,[D_h(T_1) - D_h(T_2)]\mu t/\cos\theta\,, \tag{2}$$

where t is the thickness of the crystal plate.

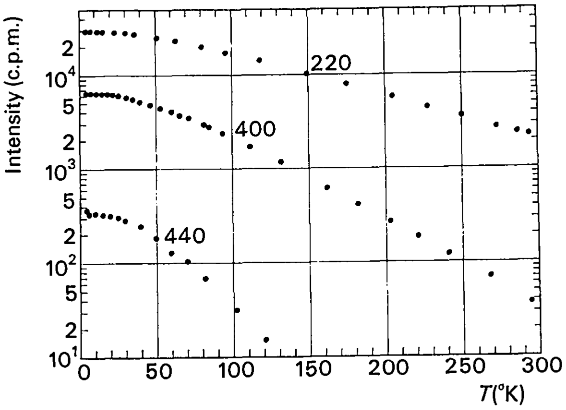

Fig. 1. Relative intensity (log I) *vs* temperature T curves of three Ge reflexions; Mo $K\alpha$, $\mu t = 96$.

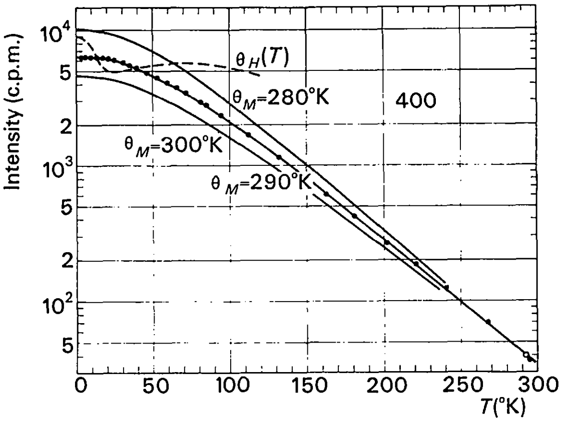

Fig. 2. Ge 400 intensity calculated with 3 constant values of the characteristic temperature Θ_M. Black dots: experiment. Broken line: calculated with Θ_H (specific heat data of the characteristic temperature).

Let us repeat: (2) gives an approximation of what happens in the crystal, and is in fact a surprisingly good approximation as will be shown below. We chose $\mu t = 96$. The formula explains a main feature of the experiments, the large variation in the intensity.

Two modes of polarization must be distinguished. The least absorbed Ewald wave is perpendicularly polarized. With $\mu t = 96$ all the contributions of the parallel component of the radiation become immeasurably small. This is of course necessary for the application of the simple formula (2).

The present state of knowledge

The method was applied to Ge by Batterman (1962) and (1964), Okkerse (1962), Ling & Wagenfeld (1965), Ghezzi, Merlini & Pace (1967), Efimov (1967); to Zn by Merlini & Pace (1965); to Cu by Baldwin, Young & Merlini (1967), Baldwin (1968). The temperature range investigated in the case of Ge was 80–650°K. Lower temperatures seemed to be interesting for two reasons. We wished to prove the validity of the dynamic theory under extreme conditions, and to find out whether the Debye temperature Θ is constant or not. At room temperature, above and below it, a marked difference was found between Θ_H determining the specific heat, and Θ_M valid for $D_h = e^{-M}$: $\Theta_H = 354\,°\text{K}$, $\Theta_M = 290\,°\text{K}$ (Batterman). What remained to be done were X-ray diffraction measurements of any kind at 20°K, where Θ_H has a deep minimum [see Blackman (1955)]. The question was how Θ_M would behave at that temperature. According to Batterman & Chipman's (1962) calculations no minimum was expected but a very faint maximum instead ($\Theta_M = 296$; 312; 310°K at $T = 293$; 20; 0°K respectively).

Experiments

The intensity of three Ge reflexions was measured with a scintillation counter while the temperature of the crystal was gradually lowered from 293 to about 5°K. The experimental conditions were as follows: Mo $K\alpha$ radiation, a crystal disc of extremely pure Ge without dislocations, ground, polished, and etched, $t = 0{\cdot}299$ cm thick, absorption coefficient $\mu = 321\ \text{cm}^{-1}$, $\mu t = 96$, symmetric Laue case of interference. In most cases both components of the Ewald waves were measured. Their intensity ratio I_h/I_0 agreed (to within an experimental error of about $\pm 0{\cdot}03$) with the value 0·98 demanded by the dynamic theory. This agreement may be considered as a proof that there was no temperature gradient in the crystal. Details are given elsewhere (Ludewig, 1966). The cryostat will be described by Höhne, Klipping, Ludewig, Tippe & Walter (1968).

Results

Fig. 1 shows the results obtained with the 220, 400, and 440 reflexions of Ge. The log I curves start with an almost constant slope at room temperature but then turn to approach constant values. The 440 reflexion was too weak to be measured at room temperature.

Fig. 2 shows the comparison with calculated curves in the case of 400. All the experimental curves agree well with the theory if $\Theta_M = \text{constant} = 290\,^\circ\text{K}$ is assumed. There is no indication that Θ_M varies at 20°K.

Table 1 shows the intensity ratios taken from Fig. 1 together with various calculated values. In the case of 220, for instance, $D_{220}(293^\circ)=0\cdot965$, $D_{220}(5^\circ)=D_{220}(0^\circ)=0\cdot992$. With these values, formula (1) yields $I(0^\circ)/I(293^\circ)=\exp(0\cdot027\times96)=13$.

Table 1. *The intensity ratio* $I(0\,^\circ\text{K})/I(293\,^\circ\text{K})$

(a) According to formula (2); (b) according to Kato's formula of the integrated intensity. Effects of the thermal contraction of the crystal were considered. $\mu_{\min}$ values according to formula (1) with $\mu=321\text{ cm}^{-1}$.

	Experiment	Calculated (a)	Calculated (b)	$\mu_{\min}(0\,^\circ\text{K})$
220	$13\pm0\cdot4$	13·0	13·0	3·3 cm^{-1}
400	160 ± 8	161	164	6·6
440	(23 600 ± 2 000) (extrapolated)	24 200	23 900	13·6

Discussion

At present the discussion of the results given here cannot be complete. There are still questions and there are several minor effects which may more or less contribute to the attenuation of the Ewald waves. In view of the sensitivity of the method these effects should be taken care of. The complexity of the whole problem can be studied in the papers by Efimov (1967) and by Baldwin, Young & Merlini (1967). Questionable items are: The precise value of Θ_M at $T=293\,^\circ\text{K}$; Θ_M slightly changing or not; experimental values of W_h; Compton effect and thermal diffuse scattering in the case of Ewald waves; intrinsic crystal defects (except dislocations); a small temperature gradient in the crystal.

Let us look briefly at the first and second points. Starting at $T=293\,^\circ\text{K}$ with $\Theta_M=289\,^\circ\text{K}$ (instead of 290°) and then adjusting the theoretical to the experimental curves, one gets a slightly decreasing Θ_M; starting with $\Theta_M=291^\circ$, one gets a slightly increasing Θ_M. Therefore a precise value of Θ_M at room temperature is needed. 290° seemed to be a reasonable value according to the results published by several authors and to the results of numerous measurements at room temperature obtained in our laboratory (G. Hildebrandt). But Efimov used 296°, while Ghezzi, Merlini & Pace insist on $283^\circ\pm3^\circ$.

Further measurements particularly at low temperatures may be useful.

Summary

The intensity of interfering X-rays transmitted through a very thick crystal depends strongly on the temperature. When the crystal is cooled to 5°K, the intensity may increase by some orders of magnitude, in accord with the dynamic theory. The simple explanation is that the atoms of the unit cell remain closer to the nodes of the Ewald waves when their thermal vibrations diminish. Hence the probability of the photoeffect (and of very weak other attenuation effects) becomes smaller. The absorption coefficient is reduced to about 1% of its normal value ($\mu_{\min}=3\cdot3$, $\mu=321\text{ cm}^{-1}$) in the case of 220. For the special wave-field the crystal is nearly 'X-optically void' (Ewald's term; it means no refraction, no absorption).

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DISCUSSION

EWALD: Might I ask for the definition of this wave (Ewald wave)? Is it any wave where the tie-point lies on the surface of dispersion? Looked at correctly – and I meant to show this in my talk – this is just the equivalent of a proper mode and a proper tie-point. There is no reason to give it a particular name.

BORRMANN: There are many proper modes in physics.

BATTERMAN: Might I propose a possible explanation for one item. The diffuse X-ray scattering was calculated on the phonon spectrum measured at room temperature. The fact that the fit at lower temperature was less satisfactory may indicate a change of the phonon spectrum as the temperature is lowered and this could be associated with the anharmonic properties of the crystal.

CHANDRASEKHAR: At absolute zero, would $\mu_{\min}$ be zero for point atoms or for real atoms?

BORRMANN: For point atoms.