From our results, the value of the lattice parameter at 20 °C is 6·1026 Å. This compares with the values 6·085 (Horak, Machovec & Kosek, 1957), 6·102 (Zachariasen, 1926), 6·1026 (Swanson, Morris, Evans & Ulmer, 1964) and 6·1026 at 23 °C (Holland & Beck, 1968).

From the graph given by Novikova & Abrikosov (1963) the thermal-expansion coefficient at 27 °C is $8{\cdot}5\times10^{-6}\,°C^{-1}$ and our value is $9{\cdot}03\times10^{-6}\,°C^{-1}$ at 35 °C. The mean thermal expansion determined from the data of Holland & Beck (1968) is $9{\cdot}2\times10^{-6}\,°C^{-1}$ from 23 to 458 °C whereas our value is $9{\cdot}67\times10^{-6}\,°C^{-1}$ from 35 to 445 °C.

Mercury selenide

Pure mercury selenide was annealed at 150 °C for three hours. The reflexions 711, 642, and 731 were used for the derivation of the lattice parameters. The lattice parameters and the thermal expansion coefficients are given by the equations:

$$a_t = 6{\cdot}0854 + 28{\cdot}61\times10^{-6}t + 4{\cdot}93\times10^{-9}t^2 + 3{\cdot}74\times10^{-12}t^3$$

and

$$\alpha_t = 4{\cdot}70\times10^{-6} + 1{\cdot}62\times10^{-9}t + 1{\cdot}84\times10^{-12}t^2$$

respectively. Some values are given in Table 2.

Table 2. *Lattice parameters and thermal expansion coefficients of mercury selenide*

Temperature (°C)	a (Å) Observed	a (Å) Calculated	$\alpha\times10^6$ ($°C^{-1}$)
34	6·0864	6·0864	4·76
150	6·0898	6·0898	4·99
215	6·0919	6·0918	5·13
265	6·0934	6·0934	5·26
330	6·0954	6·0955	5·44
377	6·0971	6·0971	5·57

The room-temperature lattice parameter determined by Cruceanu, Nistor & Niculescu (1966) is $a=6{\cdot}088$ Å, by Bethke (1956) $a=6{\cdot}073$ Å and by Swanson, Gilfrich & Cook (1957) $a=6{\cdot}085$ Å; our value is $a=6{\cdot}0864$ Å at 34 °C.

Zhdansova *et al.* (1966) determined the thermal expansion of mercury selenide dilatometrically from 20 to 500 °K and they have plotted the thermal expansion coefficient against temperature. The value taken from their graph is about $1{\cdot}4\times10^{-6}\,°C^{-1}$ at 27 °C; our value at 34 °C is $4{\cdot}76\times10^{-6}\,°C^{-1}$ which is nearly three times greater than that of former workers. There seems to be some discrepancy here that needs investigation.

The authors express their thanks to Drs H. D. Riccius and C. Mande for providing pure zinc telluride and mercury selenide.

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Acta Cryst. (1970). A**26**, 364

Anomalous Neutron Scattering by Crystals and the Amplitudes of Vibration of Lattice Waves

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(*Received* 6 *October* 1969)

This paper deals with the scattering of neutrons by crystals which contain at least one anomalous scatterer. It is shown that anomalous scattering studies provide a powerful method of evaluating the amplitudes of lattice waves for crystals like CdS with at least one anomalous scatterer in the unit cell.

1. Introduction

It is well known that anomalous-dispersion methods provide a powerful tool for the phase determination of complex structures by X-ray scattering. If the nuclear resonance energies in a crystal are low and lie in the thermal neutron range, as in the case of substances like ^{113}Cd, ^{151}Eu, ^{149}Sm, and ^{157}Gd, strong anomalous-

dispersion effects will occur in neutron scattering. The principal effects of anomalous scattering are twofold: firstly, the scattering factor turns out to be complex and has the form

$$f=f_0+f'+if'' \tag{1}$$

where f_0 is the normal scattering factor for wavelengths far away from the resonance regions and f' and f'' are real and imaginary parts of the resonance correction; secondly, f' and f'' are dependent on the wavelengths of the incident neutrons. Since the real part f' of the correction could be five to ten times larger than the normal scattering length (Ramaseshan, 1966), Singh & Ramaseshan (1968) pointed out that the 'heavy atom' technique could be successfully exploited for neutron scattering also. Further, by making measurements at two wavelengths on either side of the resonance wavelength, the position of the anomalous scatterer could easily be determined and anomalous dispersion effects could provide a useful method for solving complex crystal structures. The scattering of neutrons by crystals has been studied by several authors, especially by Weinstock (1944), Cassels (1950) and Waller & Froman (1952) and there are excellent text books on the subject (Maradudin, Montroll & Weiss, 1963; Bak, 1964), but very little work seems to have been done on the scattering of thermal neutrons by phonons in a crystal, when the latter has an atom that scatters anomalously. It is the object of this note to present the results of such a study of the anomalous scattering of neutrons by crystals and to demonstrate the use of this method to evaluate the amplitude of the lattice waves.

2. The amplitude of the lattice waves

With the usual notation (Maradudin, Montroll & Weiss, 1963), the differential scattering cross section per unit solid angle and unit interval of outgoing energy of the scattered particle may be written as

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\mathrm{d}\varepsilon}=\frac{k}{\hbar k_0}S(\boldsymbol{\kappa},\omega) \tag{2}$$

where

$$S(\boldsymbol{\kappa},\omega)=|\sum_{n_0}P_{n0}\sum_{n}\langle n|\sum_{kl}f_k \exp[i\boldsymbol{\kappa}\,.\,\mathbf{x}(l_k)]\,|n_0\rangle|^2\delta\left(\omega+\frac{E_{n_0}-E_n}{\hbar}\right) \tag{3}$$

where

$$\hbar\omega=\frac{\hbar^2}{2m}(k_0^2-k^2)\,. \tag{4}$$

The quantities m, $\mathbf{k}_0$, $\mathbf{k}=\mathbf{k}_0-\boldsymbol{\kappa}$ are the mass and the initial and final wave vectors of the scattered neutron; the frequency ω is defined by (4). Further f_k is the scattering length of the kth nucleus and since the scattering is anomalous, it has the form

$$f_k=f_{k0}+f_k'+if_k''. \tag{5}$$

The expression (3) for $S(\boldsymbol{\kappa},\omega)$ has been evaluated using pair distribution functions in space and time as given by van Hove (1954). The final result may be written

$$S(\boldsymbol{\kappa},\omega)=\frac{N^2}{2\pi}\sum_{k_1k_2}\exp[-(W_{k_1}+W_{k_2})]f_{k_1}^*f_{k_2}\exp\{i\boldsymbol{\kappa}\,.\,[\mathbf{r}(k_2)-\mathbf{r}(k_1)]\}(J_0+J_1+J_2+\ldots)$$

where W_{k_1} and W_{k_2} are the Debye–Waller factors and

$$J_0=\delta(\omega)\Delta(\boldsymbol{\kappa}) \tag{7}$$

$$J_1=\sum_{kj}\{S_{k_1k_2}(\mathbf{k}j)\delta[\omega+\omega_j(\mathbf{k})]\Delta(\boldsymbol{\kappa}+2\pi\mathbf{k})+T_{k_1k_2}(kj)\delta[\omega-\omega_j(\mathbf{k})]\Delta(\boldsymbol{\kappa}-2\pi\mathbf{k})\}\,. \tag{8}$$

Further

$$S_{k_1k_2}=\frac{\hbar}{N\sqrt{M_{k_1}M_{k_2}}}R.[\boldsymbol{\kappa}\,.\,\mathbf{e}(k_2|\mathbf{k})_j\boldsymbol{\kappa}\,.\,\mathbf{e}^*(k_1|\mathbf{k})_j]\times\frac{[\bar{n}(\mathbf{k}j)+1]}{2\omega_j(\mathbf{k})} \tag{9}$$

$$T_{k_1k_2}=\frac{\hbar}{N\sqrt{M_{k_1}M_{k_2}}}R[\boldsymbol{\kappa}\,.\,\mathbf{e}(k_2|^{\mathbf{k}}_j)\boldsymbol{\kappa}\,.\,\mathbf{e}^*(k_1|^{\mathbf{k}}_j)]\times\frac{\bar{n}(\mathbf{k}j)}{2\omega_j(\mathbf{k})}\,, \tag{10}$$

where $\bar{n}(\mathbf{k}j)$ is the number operator associated with the phonon state (kj) and $\mathbf{e}(k_2|\mathbf{k})_j$ denotes the normalized amplitude of the lattice wave having momentum $\hbar\mathbf{k}$ and passing through the ith type of atom in the unit cell. The terms $J_0, J_1 \ldots$ represent the cross section for neutron scattering of order zero, one, two ... *etc.* and the delta factors of the type $\delta(\omega_j(\mathbf{k})+\omega)$ and $\delta(\omega_j(\mathbf{k})-\omega)$ represent emission and absorption processes.

The expression for the intensity of the diffuse scattering in the first and higher orders contains the factors $S_{k_1k_2}(\mathbf{k}j)$ and $T_{k_1k_2}(\mathbf{k}j)$ which are quadratic functions of the amplitudes $e(k_2|\mathbf{k})_j$ of the lattice waves. An analysis of the cross section of the scattering in the first and higher orders can therefore yield useful information about the amplitude of the lattice waves. For simplicity, consider a crystal with two atoms in a unit cell of which one at least is an anomalous scatter. Let us write

$$f_1=A_1\exp(i\theta_1);\quad f_2=A_2\exp(i\theta_2);\quad \boldsymbol{\kappa}\,.\,[\mathbf{r}(k_2)-\mathbf{r}(k_1)]=\boldsymbol{\kappa}\,.\,\mathbf{r} \tag{11}$$

and

$$\theta=(\theta_2-\theta_1)\,.$$

We shall also denote the intensity of the Bragg scattering corresponding to the reciprocal lattice vectors $\boldsymbol{\kappa}_0$ and $-\boldsymbol{\kappa}_0$ by I_0 and I_0^*. A simple calculation then shows that

$$\Delta I_0 = I_0^* - I_0 = \frac{4N^2}{2\pi} A_1 A_2 \exp\left[-(W_1+W_2)\right] \sin\theta \sin \boldsymbol{\kappa}_0 \,.\, \mathbf{r} \,. \quad (12)$$

Similarly, considering one-phonon processes, let us denote by I_1 and I_1^* the intensity associated with the reciprocal lattice vectors $\boldsymbol{\kappa}_1 + 2\pi\mathbf{k}$ and $(-\boldsymbol{\kappa}_1 - 2\pi\mathbf{k})$. Then again one finds

$$I_1 = \frac{N^2}{2\pi}\{A_1^2 S_{11} \exp(-2W_1) + A_2^2 S_{22} \exp(-2W_2) + 2A_1 A_2 S_{12} \exp\left[-(W_1+W_2)\right] \cos(\boldsymbol{\kappa}_1 \,.\, \mathbf{r} + \theta)\} \quad (13)$$

and

$$\Delta I_1 = \frac{2N^2}{\pi} \exp\left[-(W_1+W_2)\right] A_1 A_2 S_{12} \sin\theta \sin \boldsymbol{\kappa}_1 \,.\, \mathbf{r} \,. \quad (14)$$

From (12) and (14), it follows that

$$\frac{\Delta I_1}{\Delta I_0} = S_{12}\left(\frac{\sin \boldsymbol{\kappa}_1 \,.\, \mathbf{r}}{\sin \boldsymbol{\kappa}_0 \,.\, \mathbf{r}}\right) . \quad (15)$$

For any given $\boldsymbol{\kappa}_0$ and $\boldsymbol{\kappa}_1$ this equation at once determines S_{12}. If one writes

$$\mathbf{e}(k_1|\mathbf{k}) = P_1 \exp(i\varphi_1); \quad \mathbf{e}(k_2|\mathbf{k}) = \mathbf{P}_2 \exp(i\varphi_2) \,,$$
$$j \qquad\qquad\qquad j$$

then the equations (13) and (15) are sufficient to determine either $(\boldsymbol{\kappa}_1 \,.\, \mathbf{P}_1)$ or $(\boldsymbol{\kappa}_1 \,.\, \mathbf{P}_2)$ in terms of the phase difference $(\varphi_1 - \varphi_2)$ between the lattice waves passing through the atoms 1 and 2.

If the neutron scattering experiments are repeated for two crystals of the same type, such as CdS, of which one contains isotopes that scatter anomalously and the other is a normal scatterer, a comparison of the scattering experiments allows the complete determination of the quantities S_{11} and S_{22}. For normal scattering, we get an equation of the form

$$f_1^2 S_{11} \exp(-2W_1) + f_2^2 S_{22} \exp(-2W_2) = C_1 \,. \quad (16)$$

The equations (13), (15) and (16) are sufficient for the determination of S_{11} and S_{22}, and thus the squares of the quantities $\boldsymbol{\kappa}_1 \,.\, \mathbf{e}(k_1|\mathbf{k})$ and $\boldsymbol{\kappa}_1 \,.\, \mathbf{e}(k_2|\mathbf{k})$ are fully determined. From these the phase difference between the lattice waves passing through the two different atoms in the unit cell can be readily found. By analysing the peaks corresponding to the same $\mathbf{k}$ but to a different value of the momentum transfer vector, say $(\boldsymbol{\kappa}_1')$, such that $\boldsymbol{\kappa}_1' + 2\pi\mathbf{k} =$ reciprocal lattice vector, it is possible to evaluate the components of $\mathbf{e}(k_1|\mathbf{k})$ and $\mathbf{e}(k_2|\mathbf{k})$ along different vectors $\boldsymbol{\kappa}_1'$, $\boldsymbol{\kappa}_2''$ *etc.*, and from these the amplitudes can be completely determined. By extending the analysis for different values of the phonon wave vector $\mathbf{k}$, it is possible to study the variation of the amplitudes $\mathbf{e}(k_i|\mathbf{k})$ $(i=1, 2)$ with respect to the wave vector $\mathbf{k}$. The method of anomalous scattering thus provides a powerful means of evaluating the amplitudes of the lattice waves as well as their variation with respect to the phonon momentum vector $\mathbf{k}$ for non-centrosymmetric crystals.

For crystals containing more than two atoms in the unit cell, the expressions for $\Delta I_2 = (I_2^* - I_2)$ provide additional equations, from which it is possible to evaluate the wave amplitudes for simpler structures, but it is difficult to predict whether a sufficient number of equations or peaks will always be obtained to determine completely the amplitudes of waves passing through all the atoms. Nevertheless, the method provides sufficient parameters for valuable information about the wave amplitudes to be obtained.

Normally, the amplitudes of the lattice waves can be determined from the secular equation, but this requires a knowledge of the force constants as the dynamical matrix depends on these. The force constants, in turn, are determined from the lines or maxima in the first and second order Raman scattering and from the elastic constant data. The foregoing analysis suggests that anomalous scattering could supply additional equations in the force constants and enable one to determine more force constants, thereby throwing light on the binding forces between the atoms in the crystal.

In view of the potentialities of the anomalous scattering method, it would be worthwhile to devise and conduct experiments that could directly determine the amplitudes of the lattice waves.

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