

AN ASPECT OF NORMAL MODES OF VIBRATIONS IN DISORDERED CRYSTAL*

BY K. PARLIŃSKI

Institute of Nuclear Physics, Cracow**

(Received May 15, 1972; Revised paper received July 5, 1972)

The normal modes of vibrations of an ideal two compound disorder crystal $A_{0.50}B_{0.50}$ are studied. It is shown that the pure coherent density spectrum of the displacement operators for the acoustic branch at the centre of the Brillouin zone $q = 0$ is made up from the unbroadened phonon peak at the zero frequency and the phonon distribution function $g(\omega)$ of some average lattice.

1. Introduction

The study of the normal modes of vibrations of a disordered crystal lattice has been of considerable interest in recent years, both from the theoretical [1, 2] and the experimental [3, 4] points of view. The theory [1] of highly concentrated ideal disordered alloy has shown that the coherent processes can be described by phonons. However, the phonons are not ideal. They have considerable widths, which depend upon the wave vector. For very small wave vectors, in the vicinity of the centre of the Brillouin zone the theory [1] predicts that the widths of phonons tend to zero. This behaviour has recently been confirmed by measurements of the coherent slow neutron scattering on the disordered alloy $Ni_{0.55}Pd_{0.45}$ [3].

We shall consider the ideal disordered lattice which consists of two kinds of atoms at equal concentration. The interatomic potential is assumed not to depend upon the kind of atoms. The atoms are distinguished only in masses. We shall show that the coherent density spectrum of the disordered lattice can be expressed in terms of an average lattice, where the sites are occupied by atoms of average masses.

The purpose of this paper is to draw attention to another phenomenon which accompanies the coherent scattering processes of light or slow neutrons. We shall point out that for the acoustic branch at the centre of the Brillouin zone, except for the unbroadened phonon peak at the zero frequency, in agreement with the quoted theory [1] and experiment [3], there exists a very wide background which at first approximation is in fact the phonon

* Part of this work was done in the Department of Physics, University of Edinburgh, Scotland.

** Address: Instytut Fizyki Jądrowej, Radzikowskiego 152, 31-342 Kraków, Poland.

distribution function of the average lattice. Its total intensity is of the order of magnitude of the square of the mass defect. The form of the moments, which we shall calculate below, also suggests that a similar wide background of the same order of magnitude will appear for any wave vector.

2. The moments of the crystal lattice in harmonic approximation

Let us suppose that a mixture of two kinds of atoms A and B , forms a crystal lattice. We choose a unit cell and label the sites within this cell μ or ν . The address of the unit cell is denoted by n or m . For the description of the disordered lattice, it is convenient to introduce the "concentration" operator at a site $(n\mu)$ as

$$C(n\mu) = \begin{cases} 1 & \text{when the site } (n\mu) \text{ is occupied by an atom } A \\ -1 & \text{when the site } (n\mu) \text{ is occupied by an atom } B. \end{cases}$$

This permits the inverse mass of an atom to be written in the form

$$\frac{1}{M_{n\mu}} = \frac{1}{M} (1 + \varepsilon C(n\mu))$$

where

$$\frac{1}{M} = \frac{1}{2} \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \quad \text{and} \quad \varepsilon = \frac{M_B - M_A}{M_B + M_A}. \quad (1)$$

The Hamiltonian of the ordered or disordered system in harmonic approximation is easily written

$$H = \sum_{n\mu\alpha} \frac{(P_{\alpha}^{(n)})^2}{2M} (1 + \varepsilon C(n\mu)) + \sum_{\substack{nl \\ \mu\delta \\ \alpha\beta}} \Phi_{\alpha\beta}(n\mu|l\delta) u_{\alpha}^{(n)} u_{\beta}^{(l)} \quad (2)$$

where $\Phi_{\alpha\beta}(n\mu|l\delta)$ is the force constant, $u_{\alpha}^{(n)}$ is the operator of the displacement of a given atom from its equilibrium position.

We have assumed the force constants for any pair of atoms to be the same, independently of the kind of the atoms of the considered pair. This assumption seems to be reasonable, for example, for disordered systems which do not experience the order-disorder phase transition or form a solid solution in a wide range of concentrations.

To describe the vibrational behaviour to the crystal lattice, the advanced commutator Green function can be used

$$\mathcal{G}_{\alpha\gamma}^{\mu\delta}(n, l|t) = \Theta(t) \langle [u_{\alpha}^{(n)}(t), u_{\gamma}^{(l)}(0)] \rangle. \quad (3)$$

Its Fourier transform is an analytical function of the complex variable E .

The density spectrum is the most essential physical quantity. It can be obtained from the real part of (3)

$$K_{\alpha\gamma}^{\mu\delta}(n, l|\omega) = 2 \operatorname{Re} \mathcal{G}_{\alpha\gamma}^{\mu\delta}(n, l|\omega + i\eta)|_{\eta \rightarrow 0^+}. \quad (4)$$

The Green function may be expanded into an infinite series over the inverse powers of E

$$\frac{1}{i} \mathcal{G}_{\alpha\gamma}^{\mu\delta}(n, l|E) = \sum_{p=0}^{\infty} \frac{S_{\alpha\gamma}^{(2p-1)}(n|l)}{E^{2(p+1)}}. \quad (5)$$

The expansion coefficients are called the moments and are defined by two equivalent relations [5]

$$\begin{aligned} S_{\alpha\gamma}^{(2p-1)}(n|l) &= \frac{1}{2\pi} \int_0^{\infty} K_{\alpha\gamma}^{\mu\delta}(n, l|\omega^2) \omega^{2(p-1)} d\omega^2 = \\ &= \langle [\dots [u_{\alpha}(\mu|0), \underbrace{H \dots H}_{(2p-1)\text{-times}}, u_{\gamma}(\delta|0)] \rangle. \end{aligned} \quad (6)$$

In the harmonic approximation all even moments vanish, therefore we could have confined the ω -dependence of the density spectrum function to the positive values only. The second relation of (6) can be used for explicit calculation of the moment's values. This is possible, since the commutation relations between the displacement and the momentum operators and the Hamiltonian follow directly from the general properties of commutators and the basic relation $[u_{\alpha}(\mu), P_{\gamma}(\delta)] = i_m \delta_{\mu\delta} \delta_{\alpha\gamma}$.

In non-ideal crystal the configuration of atoms A and B at one place in the crystal usually differs from that at another place. However, because the considered volume of the crystal consists of a large number of atoms, the Green function can be well approximated by the statistical ensemble, which corresponds to the variety of the configurations of atoms, characterized by the concentration, the order, and the correlation in the crystal. The mathematical form of this suggestion can be shaped as the following sum over all unit cells

$$g_{\alpha\gamma}^{\mu\delta}(n, l|t) = \frac{1}{N} \sum_m \mathcal{G}_{\alpha\gamma}^{\mu\delta}(n+m, l+m|t). \quad (7)$$

This approximation expresses the condition of the homogeneity of the crystal. For a small concentration, when one kind of atoms can be treated as a set of isolated defects, this sort of approximation is of no use.

However, there exists another advantage of such an approach. The new Green function will be translational invariant throughout the whole lattice, although this does not mean that the crystal is ordered. It also implies the translational invariance of the configuration correlation functions which must be defined similarly to (7) *i. e.*

$$\begin{aligned} \langle C(\mu) \rangle &= \frac{1}{N} \sum_n C(n\mu) \\ \vdots & \\ \langle C(n\mu)C(m_1\nu_1)\dots C(l\delta) \rangle &= \\ = \frac{1}{N} \sum_m \langle C(n+m, \mu)C(m_1+m, \nu_1)\dots C(l+m, \delta) \rangle. \end{aligned} \quad (8)$$

Now, we are ready to calculate the moments in approximation (7). After some simple algebra we find

$$\begin{aligned}
 S_{\alpha\gamma}^{(1)}(n_\mu | l\delta) &= \frac{1}{M} (1 + \varepsilon \langle C(\mu) \rangle) |\delta_{nl} \delta_{\mu\delta} \delta_{\alpha\gamma} \\
 S_{\alpha\gamma}^{(3)}(n_\mu | l\delta) &= \frac{1}{M^2} \Phi_{\alpha\gamma}(n\mu | l\delta) \times \\
 &\quad \times (1 + \varepsilon \langle C(\mu) \rangle + \varepsilon \langle C(\delta) \rangle + \varepsilon^2 \langle C(n\mu)C(l\delta) \rangle) \\
 &\quad \vdots \\
 S_{\alpha\gamma}^{(2p-1)}(n_\mu | l\delta) &= \frac{1}{M^p} \sum_{\substack{m_1 v_1 \\ \beta_1}} \sum_{\substack{m_2 v_2 \\ \beta_2}} \dots \sum_{\substack{m_{p-2} v_{p-2} \\ \beta_{p-2}}} \Phi_{\alpha\beta_1}(n\mu | m_1 v_1) \times \\
 &\quad \times \Phi_{\beta_1\beta_2}(m_1 v_1 | m_2 v_2) \times \dots \times \Phi_{\beta_{p-2}\gamma}(m_{p-2} v_{p-2} | l\delta) \times \\
 &\quad \times \{1 + \varepsilon(\langle C(\mu) \rangle + \langle C(v_1) \rangle + \dots + \langle C(v_{p-2}) \rangle + \langle C(\delta) \rangle) + \\
 &\quad + \varepsilon^2(\langle C(n\mu)C(m_1 v_1) \rangle + \langle C(n\mu)C(m_2 v_2) \rangle + \dots \\
 &\quad + \langle C(m_{p-2} v_{p-2})C(l\delta) \rangle) + \\
 &\quad + \varepsilon^3(\langle C(n\mu)C(m_1 v_1)C(m_2 v_2) \rangle + \dots) + \\
 &\quad + \varepsilon^4(\langle C(n\mu)C(m_1 v_1)C(m_2 v_2)C(m_3 v_3) \rangle + \dots) + \dots \\
 &\quad \vdots \\
 &\quad + \varepsilon^p \langle C(n\mu)C(m_1 v_1) \dots C(l\delta) \rangle\}. \tag{9}
 \end{aligned}$$

These moments are valid for any degree of order and concentrations of the constituents.

Owing to the fact that the force constants do not depend upon the kind of atoms, we may introduce an average crystal lattice, where every site is occupied by an atom having the mass $M = \frac{2M_A M_B}{M_A + M_B}$. We leave the sizes of the unit cell unchanged. The dynamical matrix of the average lattice has, of course, the standard form

$$D_{\alpha\beta}^{\mu\nu}(q) = \frac{1}{M} \sum_m \Phi_{\alpha\beta}(n\mu | m\nu) e^{-iq \cdot (\binom{n}{\mu} - \binom{m}{\nu})}. \tag{10}$$

Its frequencies $\omega(qj)$ and the polarization vectors $e_\alpha^\mu(qj)$ can be found from the equation

$$\omega^2(qj) e_\alpha^\mu(qj) = \sum_{\beta\nu} D_{\alpha\beta}^{\mu\nu}(q) e_\beta^\nu(qj). \tag{11}$$

Simultaneously

$$\begin{aligned}\sum_j e_\alpha^\mu(qj)e_\beta^{*\nu}(qj) &= \delta_{\mu\nu}\delta_{\alpha\beta} \\ \sum_{\alpha\mu} e_\alpha^\mu(qj)e_\alpha^{*\mu}(qj') &= \delta_{jj'}.\end{aligned}\quad (12)$$

All moments can be expressed in terms of these characteristics. To do this, we should substitute the force constants

$$\Phi_{\alpha\beta}(n\mu|mv) = \frac{M}{N} \sum_{qj} e_\alpha^\mu(qj)e_\beta^{*\nu}(qj)\omega^2(qj)e^{iq\cdot((\mu^n) - (\nu^m))} \quad (13)$$

into the expression for the moments (9) and perform appropriate summations.

Let us define the Green function of coherent processes as

$$g_{\text{coh}}(E, qj) = \sum_l \sum_{\substack{\mu\delta \\ \alpha\beta}} e_\alpha^{*\mu}(qj)g_{\alpha\gamma}^{\mu\delta}(n, l|E)e_\gamma^\delta(qj)e^{-iq\cdot((\mu^n) - (\delta^l))}. \quad (14)$$

This function can also be expanded into a series over the inverse E , similarly to (5). The expansion coefficients are new moments. To calculate them, we may use the previously defined moments (9) and apply the same transformation as in the definition (14).

3. The dynamics of the crystal lattice of the ideal disordered $A_{0.50}B_{0.50}$ alloy

Now, we shall confine our considerations to the alloy $A_{0.50}B_{0.50}$ of two kinds of atoms of equal concentrations. We choose the unit cell so that it consists of two equivalent sites. We also assume that the crystal is ideal disordered. In the language of correlation functions this assertion means that all odd correlation functions vanish

$$\begin{aligned}\langle C(\mu) \rangle &= 0 \\ \langle C(n\mu) C(m\gamma) C(l\delta) \rangle &= 0 \\ \text{etc.}\end{aligned}\quad (15)$$

and the even ones are some combinations of Kronecker's delta. For example, the two particles correlation function is

$$\langle C(n\mu)C(l\delta) \rangle = \delta_{nl}\delta_{\mu\delta}. \quad (16)$$

Any correlation between a pair of different particles disappears. Under these conditions the moments which correspond to the coherent Green function (14) can be found, using the characteristics of the average lattice. We present only the approximated expressions

for them

$$\begin{aligned}
 S^{(1)}(qj) &= 1 \\
 S^{(3)}(qj) &= \omega^2(qj) + \varepsilon^2 r_2(qj) \\
 &\vdots \\
 S^{(2p-1)}(qj) &= \omega^{2(p-1)}(qj) + \\
 &+ \varepsilon^2 \sum_{k=1}^{p-1} (p-k) [\omega(qj)]^{2(p-k-1)} r_{2k}(qj)
 \end{aligned} \tag{17}$$

where

$$\begin{aligned}
 r_{2l}(qj) &= \sum_{\mu} \sum_{\alpha\gamma} e_{\alpha}^{*\mu}(qj) \mu_{2l}(\mu, \alpha\gamma) e_{\gamma}^{\mu}(qj) \\
 \mu_{2l}(\mu, \alpha\gamma) &= \frac{1}{N} \sum_{qj} e_{\alpha}^{\mu}(qj) \omega^{2l}(qj) e_{\gamma}^{*\mu}(qj) = \\
 &= \int_0^{\infty} \omega^{2l} p_{\alpha\gamma}^{\mu}(\omega^2) d\omega^2.
 \end{aligned} \tag{18}$$

The moments have been calculated up to ε^2 . All terms of the order ε^4 , ε^6 and higher have been neglected. Note that the ε^4 term contributes to the moments $S^{(2p-1)}$, for $p \geq 4$. The ε^6 term appears for the first time in $S^{(11)}$.

The function $p_{\alpha\gamma}^{\mu}(\omega^2)$ describes the phonon distribution function for an atom μ and the correlation of directions α and γ . Its definition is

$$p_{\alpha\gamma}^{\mu}(\omega) d\omega = \frac{1}{N} \sum_{\substack{qj \\ \omega + d\omega > \omega(qj) > \omega}} e_{\alpha}^{\mu}(qj) e_{\gamma}^{*\mu}(qj) \tag{20}$$

which is very similar to the definition of the phonon frequency distribution $g(\omega)$. We also have the normalization condition

$$\int_{-\infty}^{\infty} p_{\alpha\gamma}^{\mu}(\omega) d\omega = \delta_{\alpha\gamma} \tag{21}$$

which is the consequence of the relation (12).

Knowing all the moments (17), we might have found the coherent spectral density function using the method of moments [5]. However, we are not able to find the solution until the moments are calculated exactly, including all terms of the needed order of ε . The region of very small frequencies $\omega(qj)$ is an exception. When we put $\omega(q = 0, \text{acoustic branch}) = 0$ then the moments prove to be proportional to the corresponding moments

of the phonon distribution of the average lattice, multiplied by ε^2 . Thus, from (17) we have

$$\begin{aligned} S^{(1)}(q = 0, \text{ acoustic b.}) &= 1. \\ S^{(3)}(q = 0, \text{ acoustic b.}) &= \varepsilon^2 r_2(q = 0, \text{ acoustic b.}) \\ &\vdots \\ S^{(2p-1)}(q = 0, \text{ acoustic b.}) &= \varepsilon^2 r_{2(p-1)}(q = 0, \text{ acoustic b.}) \end{aligned}$$

for $p \geq 2$. (22)

It is easy to see that these moments are generated by the following coherent spectral density function

$$\begin{aligned} K_{\text{coh}}^{(\text{approx})}(q = 0, \text{ acoustic b.}|\omega^2) &= \\ &= 2\pi\{(1-\varepsilon^2)\delta(\omega^2) + \varepsilon^2 \sum_{\mu} \sum_{\alpha\gamma} e_{\alpha}^{*\mu}(q = 0) P_{\alpha\gamma}^{\mu}(\omega^2) e_{\gamma}^{\mu}(q = 0)\}. \end{aligned} \quad (23)$$

We also note that the true K_{coh} will contain terms proportional to $\varepsilon^4, \varepsilon^6$ etc. but the suitable generating function is not so easy to find. Let us denote a generating function of the order ε^4 by $f(\omega^2)$. From the general form of the moments (6) and (9) we see that this function must obey

$$\begin{aligned} \varepsilon^4 \int_0^{\infty} f(\omega^2) d\omega^2 &= 0 \\ \varepsilon^4 \int_0^{\infty} f(\omega^2) \omega^2 d\omega^2 &= 0 \\ \varepsilon^4 \int_0^{\infty} f(\omega^2) \omega^4 d\omega^2 &= 0. \end{aligned} \quad (24)$$

This suggests that the values of $f(\omega^2)$ oscillate around zero. A similar situation occurs for the generating functions of higher order. The contribution of a higher order than ε^2 seems to be small for small ε and therefore can be neglected.

When the considered crystal forms a lattice of a cubic structure such that the two sites of the unit cell are equivalent, then the partial phonon distribution is well approximated by the usual phonon spectrum *i. e.*

$$P_{\alpha\gamma}^{\mu}(\omega^2) \approx \delta_{\alpha\gamma} g(\omega^2). \quad (25)$$

Whence

$$\begin{aligned} K_{\text{coh}}(q = 0, \text{ acoustic b.}|\omega^2) &= 2\pi\{(1-\varepsilon^2)\delta(\omega^2) + \varepsilon^2 g(\omega^2) + \\ &+ \varepsilon^4 f(\omega^2) + \dots\}. \end{aligned} \quad (26)$$

The coherent density spectrum which corresponds to the acoustic branch consists of the δ -function at $\omega = 0$, the total intensity of which is equal to $1 - \varepsilon^2$, and the phonon spectrum of a total intensity ε^2 . The higher oscillating corrections $\varepsilon^4 f(\omega^2)$ will modulate the phonon spectrum.

This result suggests that $g(\omega)$ appears as a background in the coherent scattering process. When the system becomes ordered this effect vanishes. The region $q = 0$ is easily attainable by the Raman experiment. However, the data would be deformed slightly by the scattering on the optical mode at $q = 0$.

Deeper analysis of the form of the moments suggests that the non-interacting phonons do not exist in the disordered system. We can, however, classify the states of the coherent density function $K_{\text{coh}}(q, j|\omega^2)$ by a wave vector q and the number of a dispersion phonon branch. The shape of $K_{\text{coh}}(q, j|\omega^2)$ for fixed q and j suggests the existence of a phonon around the corresponding frequency of the average lattice with a finite width and a very wide background, the total intensity of which is of the order ε^2 .

The author expresses his gratitude to Professor R. A. Cowley for drawing his attention to the problem of disordered systems and for fruitful discussions and to Professor J. A. Janik for helpful interest.

Thanks are also due to the University of Edinburgh for financial support.

REFERENCES

- [1] D. W. Taylor, *Phys. Rev.*, **156**, 1017 (1967).
- [2] R. A. Cowley, *Symposium on Neutron Inelastic Scattering IAEA*, Vienna 1972, IAEA/SM-155/G-1.
- [3] W. A. Kamitakahara, B. N. Brockhouse, *Symposium on Neutron Inelastic Scattering IAEA*, Vienna 1972, IAEA/SM-155/A-6.
- [4] W. J. L. Buyers, R. A. Cowley, *Symposium on Neutron Inelastic Scattering IAEA*, Vienna 1968, vol. I, p. 43.
- [5] K. Parliński, *Acta Phys. Polon.*, **A39**, 507 (1971).