Resonance phenomena in a phonon subsystem in connection with anomalies of the structural state of metals

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Anomalies in the quasielastic scattering of neutrons in crystals may be caused by resonances in the phonon spectrum. For example, the features recently observed in the structural state of potassium are interpreted as charge-density waves which are associated with a 1:3 multiple relationship between phonon frequencies at the corresponding point in the Brillouin zone and a synchronization ("locking") of the phases of phonons. Manifestations of locking in lattice dynamics are discussed (a splitting of phonon frequencies and the threshold nature of quasielastic scattering) in the example of the bcc phases of K and Zr. Anomalies are predicted in the quasielastic scattering of bcc and fcc metals.

Giebultowicz *et al.*[1] have observed peaks in the quasielastic scattering of neutrons in K near the point $\mathbf{Q}_0 = (0.995,0.975,0.015)2\pi/a$, where a is the lattice constant, with an intensity on the order of 10^{-5} of that of the Bragg peaks. Their interpretation of these peaks as a manifestation of a charge-density wave[1] came under criticism,[2] since there are serious experimental objections to the existence of charge-density waves in alkali metals.[2,3] In the present letter we show that the effects observed by Giebultowicz *et al.*[1] may be related to a multiple relationship between frequencies $\omega_\nu(\mathbf{Q}_0)$ and the appearance of a pronounced "coupling" of corresponding phonons: a resonance in the phonon subsystem. A calculation of $\omega_\nu(Q_0)$ in the theory of Ref. 4, which gives a

precise description of the lattice dynamics of K, yields $\omega_1 = 2.474$ K, $\omega_2 = 4.541$ K, $\omega_3 = 7.398$ K, and $\omega_3/\omega_1 = 2.990$, so that neutron scattering processes accompanied by the emission of a phonon with a frequency ω_3 and the simultaneous absorption of three phonons ω_1 would appear as a quasielastic scattering within an error of an energy transfer of 0.02 K (which is far smaller than the error in the selection of elastic processes in Ref. 1: 0.7 K). A calculation of the mean square displacement at the point $\mathbf{Q}_0$ at the temperature $T = 4.2$ K yields $\mathbf{Q}_0^2 \langle x^2 \rangle_{\mathbf{Q}_0} \equiv \eta \approx 0.6$. Four-phonon processes with momenta $\mathbf{q}_i$ from a small $\mathbf{q}$-space region Γ near $\mathbf{Q}_0$, in which the relation $\omega_3(q) \approx 3\omega_1(\mathbf{q})$ holds within the experimental error[1] ($\Delta\omega \lesssim 0.7$ K), contribute above the background in quasielastic scattering. The corresponding contribution[5] to the structure factor $S(\mathbf{q})$ on the order of $\eta^4\Gamma^3 \sim 0.1\Gamma^3$ is negligible (according to the calculations, $\Gamma \lesssim 10^{-8}$). The situation changes fundamentally when allowance is made for the interaction of phonons, which is characterized by an amplitude $V_{1113}(\mathbf{Q}_0,\mathbf{Q}_0,\mathbf{Q}_0,\mathbf{Q}_0) \approx 7.5 \times 10^{-4}$ [the calculations are carried out as in Ref. 6; the phonon frequencies are then expressed in units of the ion plasma frequency ω_{pi}; the ion displacements are expressed in units of $a/2\pi$; and the amplitudes of three- and four-phonon processes are expressed in units of $(2\pi/a)M\omega_{pi}^2$ and $(2\pi/a)^2 M\omega_{pi}^2$, respectively, where M is the ion mass]. This interaction can lead to a synchronization ("locking") of phases.[7,8] As a result of this locking (1) the phonons are "coupled" and cannot be treated as independent, and (2) the condition $3\omega_1 = \omega_3$ holds over the entire region of $\mathbf{q}$ space. Examples of phase locking in terms of both frequency and wave vector are known.[8] It might be suggested that both processes occur in this case, since this entire region "contracts to a point" in $\mathbf{q}$, giving rise to a δ-function contribution to $S(\mathbf{q})$. The criterion for phase locking is (see the calculations below for the case $\omega_2 = 2\omega_1$)

$$|3 - \omega_3/\omega_1| \lesssim |V_{1113}| \langle x^2 \rangle / 6\omega_1^2 \approx 0.2 . \qquad (1)$$

This condition is satisfied in a part of $\mathbf{q}$ space which is stretched out along the $[\pm 1,0,0]$ direction (according to the calculations), with a volume $\bar{\Gamma} \gg \Gamma$. Since the phonons are strongly correlated under phase-locking conditions, it is natural to suggest that we have $\delta S(\mathbf{q}) \sim \eta^4 \bar{\Gamma} \delta(\mathbf{q} - \mathbf{Q}_0)$. From Ref. 1 we would then have $\bar{\Gamma} \sim 10^{-4}$.

The instability of the ordinary state of a gas of independent phonons in the case of a multiple relationship between frequencies can be studied in the simple example of a system of acoustic phonons described by the Lagrangian

$$L = \frac{1}{2}(u_t^2 - c^2 u_x^2 + v_t^2 - 9c^2 v_x^2) - \lambda u_x v_x^3 , \qquad (2)$$

where t and x are the time and space variables, $u_t = \partial u/\partial t$, etc. Using the methods of Ref. 9, we can show that an instability will occur in the system, depending on the phase relations among the interacting wave; i.e., a state with random phases will be unstable. At the same time, we can use a variational principle to construct a state in which the amplitude and phase of wave u determine the amplitude and phase of wave v. In a calculation of the phonon Green's function in an anharmonic perturbation theory,[6] the subtle phase relations responsible for the parametric instability are lost. In this sense, the situation is analogous to Anderson localization.[10]

It follows from the proposed explanation for the data of Ref. 1 that similar effects should be observed in all alkali metals (with the possible exception of Li, because of the martensitic transition), near the same $\mathbf{Q}_0$. For example, in the model of Ref. 11, which gives a good description of $\omega_\nu(\mathbf{q})$ for all alkali metals, we have the following values for $\omega_3(\mathbf{Q}_0)/\omega_1(\mathbf{Q}_0)$: 3.04 for Na, 3.01 for K, 2.99 for Rb, and 2.97 for Cs. On the other hand, the parameters of the charge-density wave in alkali metals—if it is assumed to exist—must be different because of the differences in the electron density.

A phase locking in a situation with a resonance in the phonon subsystem seems to also be important in other cases of quasielastic scattering in metals, e.g., the "ω-like" scattering[12] in bcc Zr[12], associated with the point $\mathbf{Q}_L = (2/3,2/3,2/3)2\pi/2$. We begin our analysis of phase locking near $\mathbf{Q}_L$ with K, which is the simplest representative of a bcc metal. In K, the values of $\omega_\nu(\mathbf{Q}_L)$ at $T = 4.2$ K are[4] $\omega_1 = 0.27 \pm 0.01$ and $\omega_2 = \omega_3 = 0.55 \pm 0.01$; i.e., we have $\omega_2/\omega_1 = 2$. It may be that a phase locking will arise near $\mathbf{Q}_L$, and a peak will be observed in the quasielastic scattering. The important amplitudes are $V_{112}(\mathbf{Q}_L,\mathbf{Q}_L,\mathbf{Q}_L) \approx 0.1, |V_{113}(\mathbf{Q}_L,\mathbf{Q}_L,\mathbf{Q}_L)| \sim 10^{-5}$ ($3\mathbf{Q}_L$ is equal to the reciprocal-lattice vector). The displacements u and v satisfy the equations

$$\ddot{u} + \omega^2(-i\nabla)u + 2\gamma(-i\nabla)\dot{u} + \frac{1}{2}V_{112}v^2 = 0$$
$$\ddot{v} + \Omega^2(-i\nabla)v + 2\Gamma(-i\nabla)\dot{v} + V_{112}uv = 0, \tag{3}$$

where $\omega(\mathbf{q}),\Omega(\mathbf{q}),\gamma(\mathbf{q}),\Gamma(\mathbf{q})$ are the phonon frequencies and phonon damping, and $\omega = 2\Omega + \nu, |\nu| \ll \omega$. We seek a solution in the form

$$u(\mathbf{r},t) = A(\mathbf{r},t)\exp\{i[\mathbf{Q}_L\mathbf{r} - \omega(\mathbf{Q}_L)t]\} + B(\mathbf{r},t)\exp\{i[\mathbf{Q}_L\mathbf{r} + \omega(\mathbf{Q}_L)t]\}$$
$$+ \text{complex conj.}$$
$$v(\mathbf{r},t) = C(\mathbf{r},t)\exp\{i[\mathbf{Q}_L\mathbf{r} + \omega(\mathbf{Q}_L)t/2]\} + D(\mathbf{r},t)\exp\{i[\mathbf{Q}_L\mathbf{r} - \omega(\mathbf{Q}_L)t/2]\}$$
$$+ \text{complex conj.} \tag{4}$$

Considering only the resonance terms, assuming that A, B, C, and D are independent of $\mathbf{r}$ (for simplicity, eliminating effects of a spatial-modulation type), we transform from (3), (4) to the system

$$\partial r/\partial t + \gamma(r - r_0) + \Lambda R^2 \sin\Phi = 0,$$
$$\partial R/\partial t + \Gamma(R - R_0) - 4\Lambda R r \sin\Phi = 0, \tag{5}$$
$$\partial\Phi/\partial t + \nu + \Lambda(R^2/r - 8r)\cos\Phi = 0.$$

Here $r = |A|$, $R = |C|$, $\Phi = \arg A + 2\arg C$, $\Lambda = V_{112}/4\omega$ (all quantities are taken at the point $\mathbf{Q}_L$). To take the interaction with the reservoir into account in the simplest way, we have introduced in (5) the terms $-\gamma r_0$ and $-\Gamma R_0$, which impose a relaxation to thermodynamic-equilibrium values of the amplitudes, r_0 and R_0, in the case $\Lambda = 0$. It can be shown that the solution corresponding to a frequency locking, $\Phi = \text{const}$, exists if

$$|\nu| < |\Lambda(R_0^2/r_0 - 8r_0)|. \tag{6}$$

so that we have $|\nu/\omega| \lesssim |V_{112}|\langle x^2\rangle^{1/2}/\omega^2 \sim 10^{-2}$ at $T = 4.2$ K. It follows from this estimate that, when we allow for the results of Ref. 6 on $\omega_\nu(\mathbf{Q}_L, T)$, the phase locking should be preserved over the interval $\Delta T \lesssim 10$ K if it is reached at a temperature which is not too low and over the interval $\Delta T < 40$–50 K if it is reached at $T = 0$. Since the phase locking does not affect $\omega_3(|V_{113}| \ll |V_{112}|)$, it should lead to a splitting of $|\omega_2 - \omega_3|/\omega_3$ by $\sim 1\%$. No secondary phase locking of ω_2 and ω_3 occurs, since the condition for the locking is

$$|V_{2233}|\langle x^2\rangle/\omega^2 \gtrsim |\nu/\omega|, \tag{7}$$

and an estimate of the left side of (7) yields 10^{-4} ($V_{2233} \approx 5 \times 10^{-2}$). If the experimental splitting is insufficient, the splitting will be perceived as a broadening. An indication of a phase locking at $\mathbf{q} \approx \mathbf{Q}_L$ in alkali metals apparently comes from the flattening of $\omega_\nu(\mathbf{q})$ and their broadening at $\nu = 2$, 3, as observed in Na (Ref. 11).

Phase locking may also explain such anomalous properties of bcc Zr (Ref. 12) as the coincidence of the transverse branches in the [110] direction and the peaks in the quasielastic neutron scattering at $\mathbf{q} \approx \mathbf{Q}_L$. In Zr, we have an experimental ratio $\omega_2(\mathbf{Q}_L)/\omega_1(\mathbf{Q}_L) \gtrsim 3$ at $T = 1423$ K, and it follows from calculations[6] and experiments[13,14] for bcc metals that this ratio decreases with decreasing T, approaching 3. The phase-locking condition apparently holds at $T \approx 1340$ K, at which a significant quasielastic scattering arises.[12] An estimate of V_{1113} in bcc Zr in a model like that of Ref. 11 yields ≈ 0.1, which is two orders of magnitude greater than V_{1113} in K. The threshold nature of the T dependence of the quasielastic scattering in Zr (Ref. 12) cannot be explained by other models for quasielastic scattering (of a central type).[15] A ratio $\omega_2(\mathbf{Q}_L)/\omega_1(\mathbf{Q}_L) \approx 3$ has also been observed[16] in bcc Tl, and a value $\omega_2(\mathbf{Q}_L)/\omega_1(\mathbf{Q}_L) \approx 2$ has been observed[17] in Sr. If these relations can be satisfied very accurately by varying the external parameters, an additional quasielastic scattering will arise, at least at high T, where $\langle x^2\rangle_{\mathbf{Q}_L}$ is not too small. The point $\mathbf{Q} = (1/2, 1/2, 1/2)2\pi/a$ in Ca (Ref. 18), Yb (Ref. 19), and Sr (Ref. 14) serves as an example of a resonant relation between phonon frequencies in fcc metals. In this connection, it would be desirable to carry out experiments on quasielastic scattering in these metals.

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