Local phonon modes and structural instability in linear defects

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The oscillation spectrum of linear defects is examined. The possible solutions of $\omega^2(q\neq 0)=0$ corresponding to the instability are investigated. The nature of the instability and the possibility of a structural transition are analyzed. The results are used to analyze the spin-lattice relaxation and the variation of the electrical resistance and specific heat.

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The presence of linear defects in the crystal lattice may lead to formation of phonon modes which are localized in the plane perpendicular to the defect.[1] Their spectrum is determined by the equation

$$\left|\delta_{\alpha\beta} - U_q^{\alpha\gamma} G_q^{0\gamma\beta}(0, \omega^2)\right| = 0. \tag{1}$$

Here $\widehat{G}_q^0(n_\perp,\omega^2)$ is the time and space (with respect to the coordinate along the line of defects and q is the corresponding wave vector) Fourier component of the Green's function for an ideal crystal and U_q is the defect-induced perturbation, which is assumed to be localized in the dislocation atoms [Lifshitz-Kosevich model,[1] $n_\perp = 0$ in Eq. (1)]. The advantage of this is that $G_q^{0\gamma\beta}$ is a tensor of second rank for the indices $\gamma\beta$ and like $U_q^{\alpha\gamma}$, is diagonalized when the defect line is selected along sufficiently symmetric directions. The bound states of interest appear at $U_q<0$, which corresponds to a decrease in interaction of the defective atoms with each other (or with the neighboring matrix atoms) as compared with the interactions in the matrix. An analysis of the dispersion equation shows that in the harmonic approximation the $\omega^2(q)$ spectrum softens (as compared with the undistorted dispersion law) and at perturbations $|U_q|$ exceeding a certain characteristic value a "roton" collapse occurs and ω^2 becomes zero at $q=q^*\neq 0$. In this paper we investigate the "roton" singularity and instability at $q=q^*$ and their manifestations in certain physical effects.

First, we analyze the possibility of solving Eq. (1) with $\omega^2(q^*)=0$. To do this, we use the model of the cubic crystal with the interaction of the nearest neighbors and the defect line along the [100] direction. We obtain from Eq. (1) at $\omega^2=0$ (for any $\phi_q^{\alpha\alpha}\neq 0$)[1]:

$$1 = \lambda \frac{x}{1+x} \mathcal{K}\left(\frac{1}{1+x}\right), \quad \lambda = -\frac{2}{\pi}\frac{\Delta\Phi}{\Phi_0}, \quad x = \sin^2\left(\frac{qa}{2}\right), \tag{2}$$

where $\Delta\Phi/\Phi_0$ is the relative variation of the force constants, $\mathcal{K}$ is the total elliptic integral, and a is the lattice constant. The value λ characterizes the perturbation

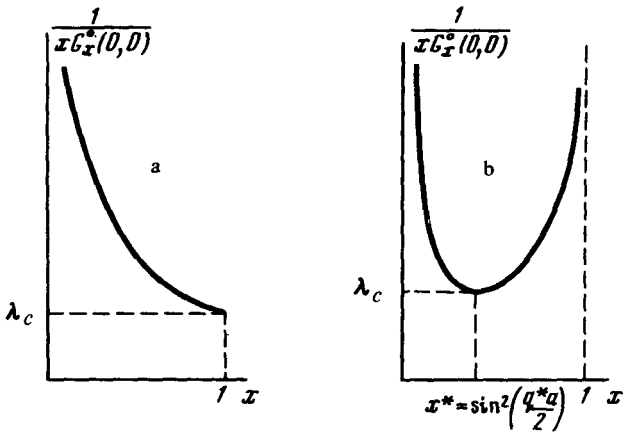

FIG. 1.

($U_q \sim \lambda x$). Figure 1(a) is a graphic solution of Eq. (2) and Fig. 1(b) is a solution of an analogous equation for the [111] direction of the defect. There are solutions at $\lambda \geqslant \lambda_c$ [for Eq. (2) $\lambda_c = 1.85$], i.e., the spectrum $\omega^2 (q \neq 0) = 0$ becomes unstable. The dependence of q^* of the corresponding λ_c on the orientation of the defect is typical: if the maximum wave vector along the defect q_m falls on the surface [as in Eq. (2)] or on the edge of the Brillouin zone, then $q^* = q_m$; if however, the defect is oriented in such a way that q_m falls on the peak of the Brillouin zone, then $q^* < q_m$.[2)]

To obtain the dependence $\omega^2(q)$ in the instability region, we must obtain anharmonic corrections for the spectrum. It is convenient to use the Green's temperature analogous to those described in Ref. 2. In contrast to the standard case, we now consider the harmonic system of the defective crystal to be unperturbed. The self-energy corrections due to the third- and fourth-order anharmonicity are:

$$\Sigma = \Omega + \text{(bubble)} . \tag{3}$$

The calculations using the Green's function for the atoms on the defect line shown in Ref. 3 give the following equation for the gap $\Delta^2 = \Omega^2(Q^*)$ (the values given below are dimensionless $\Omega = \omega/\omega_m$, $Q = q/q_m$, $t = T/\Theta$, and ω_m and Θ are the frequency and the Debye temperature):

$$\Delta^2 = \Omega_0^2(Q^*) + \alpha \begin{cases} t/\Delta, & t >> \Delta \\ \ln \dfrac{1}{\Delta}, & t << \Delta \end{cases} . \tag{4}$$

Here $\Omega_0^2(Q^*)$ is the seeding gap [(at $\lambda > \lambda_c$) it is negative: $\Omega_0^2(Q^*)^0 \equiv \Omega_0^2 = -\Delta_0^2$] and $\alpha = \Theta/\epsilon_a \sim 10^{-2}$ is the anharmonic parameter (ϵ_a is of the order of the atomic energy); the numerical factors ~ 1 in Eq. (4) were dropped.

Since there are no phase transitions in the one-dimensional systems, we conclude that $\Delta \neq 0$ (at $T = 0$ the transition is destroyed by the zero-point vibrations); the finite quantity Δ^2 describes the renormalized "roton" gap. The specific form of its tempera-

ture dependence is determined by the ratio of the parameters t, α, and Ω^2, the last of which is connected with λ in a rather complex way. The stuctural transition, however, can occur in the presence of defects. The situation for a system of parallel defects or those oriented along the crystallographically equivalent directions can be easily analyzed. In this case Δ on the right-hand side of Eq. (4) can be replaced by $\sqrt{\Delta^2 + c}$ (c is the concentration of the defect lines), which makes it possible to have solutions $\Delta = 0$ and hence a structural transition at $t_c = \sqrt{c}(\Delta_0^2/a)^2$. In the vicinity of the transition $\Delta \sim (t = t_c)^{1/2}$. This transition is accompanied by a shift of the defective atoms and by the formation of a superstructure on the line with a period $2\pi/q^*$. As shown above, the period can be doubled and in general increased incommensurably with respect to the original, depending on the orientation of the defects. We note that the short-range order can be determined at $t > t_c$: the correlator of the displacement of the defective atoms

$$< u(n_x)u(n_x') > \sim \Delta^{-1} \times \exp\left(-\frac{|n_x - n_x'|}{r_c}\right),$$

where the correlation radius $r_c = a\Delta^{-1}$ may exceed the length of the defect for sufficiently small Δ.

We used the Lenard-Jones model for interaction of atoms to determine whether the values $\lambda > \lambda_c$ can be obtained. If the spacing between the defective atoms is greater than there would be spacing in the self-matrix, then the required values of λ are theoretically possible. Note that this parameter can be changed by an external load.

Our-model of structural instability can be used for impurity-atom chains which locally vary the force matrix. We can also include in this the breaking and rearrangement of some bonds due to introduction of dislocations. Specifically, an exchange interaction,[4] which contributes to λ, take place between the "dangling" bonds.

We calculated the effects, contributed by the "roton" singularity to the dependence T of the spin-lattice relaxation time of the dislocation chain of spins τ, of the dislocation contribution to the electrical resistance ρ_d and of the specific heat C_d. Let us give some results. The spin-lattice relaxation is particularly clear namely because the local phonons participate in it. Even in the absence of a "roton" gap in the spectrum the ordinary T dependence of the Raman scattering ($\tau_k^{-1} \sim T^7$) weakens substantially and τ_k^{-1} increases. For a relaxation produced by a modulated exchange interaction we have

$$\tau_k^{-1} \approx 4 \cdot \times 10^4 A(T), \quad A(T) \approx \kappa^{-1} e^{-\kappa}, \quad \kappa = \frac{3}{2}\left(\frac{2}{\lambda t^2}\right)^{1/3}. \tag{5}$$

A gap may yield a much larger contribution. In particular when $\lambda > \lambda_c A(T) \approx \sqrt{t}\Omega_0^{-3/2} \exp(-\Omega_0/t)$. There is both qualitative and quantitative [when we set $\Omega_0 \equiv \Omega_0(Q^*) \sim 0.2$] agreement with the experiment.[4] The region in which direct relaxation processes dominate is of interest; if $\Phi < \Omega_s$ of (Zeeman frequency), $\tau_d^{-1} \sim (\Omega_s^2 - \Delta^2)^{-1/2}$.

The "roton" part of the spectrum gives the following contribution to the electrical resistance:

$$r(T) = \frac{\rho_d(T) - \rho_d(0)}{\rho_d(0)} \approx a \frac{t}{\Delta} \Gamma\left(\frac{5}{2}, \frac{\Delta}{t}\right) \tag{6}$$

(the effect of the long-wave part of the spectrum was investigated in Ref. 3). The contribution to the specific heat at $t > \Delta$ is

$$C_d \approx 3N_d\Delta \tag{7}$$

(N_d is the number of defective atoms). It follows from Eqs. (4) and (7) that the ratio of the atomic specific heats for the defect and the matrix is $\sim 15\pi^{-4}\,[\Delta_0/\alpha t^2]^{-1} \gg 1$ at sufficiently low temperatures.

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[1)]The dispersion equation (1) in the nearest-neighbor model for the isotopic impurity chain was analyzed by Iosilevskiĭ.[5] In this case, however, the perturbation is $\sim\omega^2$ and thus the effects of interest are missing.

[2)]This is attributable to the fact that in the first case $G^0_{q_n}(0,\omega^2 \neq 0$ and the right-hand side of Eq. (2) varies monotonically, whereas in the second case $G^0_{q_m}(0,\omega^2) = 0$ [because in the calculation of $G^0_{q_m}(0,\omega^2)$ the integration range of the $G^0_{qq_1}(\omega^2)$ function for the transverse momenta degenerates for $q = q_m$ to a point] and the right-hand side of function analogous to Eq. (2) has a maximum.

[1]A.M. Kosevich, Osnovy mekhaniki kristallicheskoĭ reshetki (Principls of Mechanics of Crystal Lattice), Nauka, M., 1972.
[2]V.G. Vaks, Vvedenie v mikroskopicheskuyu teoriyu sengetoelektrikov (Introduction to the Microscopic Theory of Ferroelectric Crystals), Nauka, M., 1973.
[3]V.M. Vinokur and V.Ya. Kravchenko, Zh. Eksp. Teor. Fiz. **74**, 702 (1978) [Sov. Phys. JETP **47**, 369 (1978)].
[4]V.A. Grazhulis, V.V. Kveder, and Yu.A. Ossipyian, Proc. of XX Ampere Congress, Tallin, 1978.
[5]Ya.A. Iosilevskiĭ, Fiz. Tverd. Tela **10**, 2531 (1968) [Sic!]