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The Influence of Defects on the Spectrum of Lattice Vibrations near Structural Phase Transition Points

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The spectral density of normal vibrations corresponding both to the soft phonon branch and to other lattice modes near the structural phase transition point in an imperfect crystal is studied within the framework of the Landau theory. The existence of static defects is shown to lead to various changes in the spectra depending on temperature substantially.. The possibilities of experimental verification of theoretical results obtained are discussed.

It is well-known[1] that the distortion of an ideal crystal lattice periodicity caused by a defect leads to the interaction between any normal vibrations being independent in the absence of a defect. Such an interaction has been considered in a number of papers, but the problem of investigation of the defect induced changes in the lattice vibration spectrum deserves a special treatment in the case of temperatures, close to a structural phase transition point. In contrast to the usual situation the influence of a defect is not restricted to neighbouring atoms but spreads to a vast region, the dimensions of which increase when approaching a transition point $T=T_c$. As a result, the defect induced changes in the lattice vibration spectrum depend strongly on a temperature evolution.

It has been shown recently that the most pronounced influence is due to the defects which cause the local ordering in their vicinity even in symmetrical phase.[2,3] Below we consider especially such defects, taking into account, for the sake of simplicity, the symmetrical phase only. We are interested here in so-called "frozen-in" (immobile) point defects unlike to ref. 4, where the influence of hopping defects on the spectrum of the order parameter vibrations has been considered.

The characteristic dimension of a region, where the defect induced ordering takes place is the correlation radius r_c of the order parameter η. As $r_c \to \infty$ when $T \to T_c$, the defect induced ordering can be described in continuous-medium approximation. The same approximation is used below for describing lattice vibrations as well. Thus we restrict ourselves to the vicinity of the center of Brillouin zone and to the vicinity of the soft mode wave vector. Besides we use an independent defect approximation which is valid in the temperature range not very close to T_c or at $Nr_c^3 < 1$, where N is the concentration of defects. In this paper the one component order parameter (non-degenerated soft mode) is considered. At the same time we take into account some other normal coordinates ξ (fully-symmetrical normal vibrations) and ζ and ψ (non-symmetrical normal vibrations.

The thermodynamic potential density depending on η, ξ, ζ and ψ had the form

$$\begin{aligned}\phi(\eta,\xi,\zeta,\psi) &= \frac{A}{2}\eta^2+\frac{B}{4}\eta^4+\frac{\mathscr{D}}{2}(\nabla\eta)^2+\tau_1\eta^2\xi \\ &+r_2\eta^2\psi^2+r_3\frac{\partial\eta}{\partial X_i}\frac{\partial\eta}{\partial X_j}\zeta+\ \dots \\ &+\frac{A_\xi}{2}\xi^2+\frac{\mathscr{D}_\xi}{2}(\nabla\xi)^2+\frac{A_\zeta}{2}\zeta^2 \\ &+\frac{\mathscr{D}_\zeta}{2}(\nabla\zeta)^2+\frac{A_\psi}{2}\psi^2+\frac{\mathscr{D}_\psi}{2}(\nabla\psi)^2 \quad (1)\end{aligned}$$

As usual we put here $A=A_0\tau$, $\tau\equiv(T-T_c)/T_c$ and other coefficients to be independent of τ. The coefficient r_2 differs from zero for any transformation properties of ψ and the coefficient r_3 differs from zero only in the case when the transformation properties of ζ are the same as those of the second rank symmetrical tensor.

The aim of the present work is to reveal the peculiarities of correlation functions $\langle\eta(\boldsymbol{k},\omega)\eta(-\boldsymbol{k},-\omega)\rangle$, $\langle\xi(\boldsymbol{k},\omega)\xi(-\boldsymbol{k},-\omega)\rangle$, . . . for the values $k\approx 0$.

In order to facilitate further explanations we remind some results of the "mode-coupling" theory. Let an x-oscillator be coupled linearly to some other y-oscillator. If the y-oscillator is overdamped and if its relaxation rate $\Omega_{\mathrm{R}y}$ is less than the eigen frequency Ω_{0x} of x-vibrations, the power spectrum of x-fluctuations $\langle x(\omega)x(-\omega)\rangle$ contains three maxima: two side ones at frequencies $\Omega\approx\pm\Omega_{0x}$ and a central peak at $\Omega=0$. In the case when both oscillators are underdamped, the spectrum of x-fluctuations contains four maxima at frequencies $\Omega\approx\pm\Omega_{0x}$ and $\Omega\approx\pm\Omega_{0y}$ if the eigen frequency Ω_{0y} of y-vibrations is less than Ω_{0x}.

Consider now the η-fluctuations spectrum. The defect of type mentioned above gives rise to static lattice distortions corresponding to η and to some other variables

$$\eta_{\mathrm{e}}(\tau)=\eta_0\frac{d}{\tau}\mathrm{e}^{(d-\tau)/\tau_{\mathrm{c}}},\ \xi_{\mathrm{e}}(\tau)\sim|\eta_{\mathrm{e}}(\tau)|^2, \qquad (2)$$

where d is the dimension of the defect core (of the order of magnitude of interatomic distance) and η_0 is the order parameter value at the point of defect location, η_0 being practically independent of temperature in the vicinity of T_{c}. Owing to these distortions the linear coupling between variables $\eta'=\eta-\eta_e$ and $\xi'=\xi-\xi_e$ takes place in symmetrical phase, whereas in a pure crystal only non-linear coupling occurs [see eq. (1)]. The term in the free energy corresponding to the linear coupling is written using Fourier-transforms of η and ξ

$$2\tau_1\sum_{\boldsymbol{k}}\eta_{\mathrm{e}}(-\boldsymbol{k}-\boldsymbol{q})\eta'(\boldsymbol{q})\xi'(\boldsymbol{k}) \qquad (3)$$

Thus, an oscillator $\eta'(\boldsymbol{q})$ is coupled linearly to a number of oscillators $\xi'(\boldsymbol{k})$. It follows from from (2) that

$$\eta_e(\boldsymbol{k})=\frac{4\pi\mathscr{D}d\eta_0}{v}\frac{1}{A+\mathscr{D}k^2}=\frac{4\pi}{v}\eta_0 d\tau_{\mathrm{c}}^2\frac{1}{1+\tau_{\mathrm{c}}^2k^2}, \qquad (4)$$

so the function $\eta_e(\boldsymbol{k})$ is practically independent of k for $k\leq r_{\mathrm{c}}^{-1}$ and decreases rapidly for $k>r_{\mathrm{c}}^{-1}$. As the number of $\xi'(\boldsymbol{k})$-oscillators is proportional to k^2 the main contribution to the η-fluctuation spectrum is due mainly to $\xi'(\boldsymbol{k})$-oscillators with $k\sim r_{\mathrm{c}}^{-1}$.

If $\xi'(\boldsymbol{k})$ correspond to an underdamped optical phonon branch lying below the soft branch then two additional side bands appear in the spectrum of η-fluctuations not too close to the transition point. As to optical phonon branches more common is the situation when they lie much higher than the soft mode branch. In this case the coupling between ξ' and η' manifests itself in the temperature dependent broadening of the soft mode line. The essence of such a phenomenon may be easily explained by consideration of two coupled oscillators x and y. If $\Omega_{0y}\gg\Omega_{0x}$ one may neglect the inertia term in the equation of y-oscillator motion when considering x-vibrations, so it is possible to treat y as a relaxator.

In our case the oscillator $\eta'(q\approx 0)$ is coupled to a number of $\xi'(\boldsymbol{k})$-oscillators (an amount of which is proportional to r_{c}^{-3}), thus the contribution of the ξ-branch to the damping constant $\Gamma_\eta=\gamma_\eta/m_\eta$ of the soft mode is approximately

$$\Delta\Gamma_\eta=\frac{\pi}{8}\frac{(4\pi\eta_0 d\tau_{\mathrm{c}}^2)^2\tau_1^2N\Gamma_\xi}{m_\xi m_\xi[(\Omega_{0\xi}^2-\Omega^2)^2+\gamma_\xi^2\Omega^2]}\times\frac{1}{\left(\tau_{\mathrm{c}}+\sqrt{\dfrac{\mathscr{D}_\xi}{\Omega_{0\xi}^2-\Omega^2}}\right)^3}\approx\frac{\pi^3}{4}\frac{\tau_1^2N\Gamma_\xi\eta_0^2d^2\tau_{\mathrm{c}}^4}{m_\xi m_\eta\Omega_{0\xi}^4\tau_{\mathrm{c}}^3}\backsim\tau^{-1/2} \qquad (5)$$

As to the estimates, the ratio $\Delta\Gamma_\eta/\Gamma_\eta$ may reach the values $0.1\sim 1$ at the boundary of applicability ($Nr_{\mathrm{c}}^3=1$) of used approximation of independent defects.

Note that the contribution of the same order of magnitude may be provided by alternating temperature gradients induced in the defect vicinity by the soft mode vibrations.[5,6] Remind also that such a type of "mode" interaction leads to the appearance of a central peak in the spectrum of η-fluctuations.[6]

Analogically a central peak appears due to coupling between the soft branch and a fully symmetrical phonon branch (if the last is overdamped and its relaxation rate $\Omega_{\mathrm{R}\xi}$ is less than the eigen frequency $\Omega_{0\eta}$ of η-vibrations.

One more example of a variable being invariant under operations of the high-symmetry group of the crystal is the mass density ϱ or dilatation $v=-\Delta\varrho/\varrho_e$. The frequency of v-

fluctuations (long wave longitudinal acoustical phonons) is substantially less than that one of the soft mode. As the acoustical branch is underdamped, the defect-induced linear coupling between the given acoustical mode $v(\boldsymbol{k})$ and the soft mode gives rise to the appearance of two narrow side maxima at the frequencies $\Omega_{sk}=\pm c_s k$. For the whole acoustical branch these maxima are superimposed forming two wide side bands at the frequencies $\Omega_s=\pm c_s/r_c$.[7] Nearly of the same value is the width of these lines. Note that the position of this line maximum has the same temperature dependence as the soft mode maximum, hence we may say that defects induce something like the additional soft mode maximum in the spectrum of lattice vibrations. Probably the maximum of such a kind has been observed experimentally in SbSJ.[8]

Discuss now the influence of defects on the spectrum of ξ-vibrations. Assume at first the eigen frequency of ξ-vibration to be far higher than the eigen frequency of the soft mode. In terms of x-, y-oscillators we investigate the influence of the low frequency oscillator (x) on the high frequency oscillator (y). The contribution of such a coupling to the damping constant of y-oscillator is quite analogous to that given above by eq. (5) with substitution Γ_η for Γ_ξ, so $\Delta\Gamma_\xi \backsim \tau^{-1/2}$. Thus, the defects can induce the temperature anomaly of the damping constant (i.e. of the line width) of high frequency optic vibrations. We know no more mechanisms which may provide temperature anomalies of such vibrations at phase transitions.

It has been shown in ref. 9 that in the case of the overdamped soft mode the defects cause the temperature dependence even of the damping constant of acoustical phonons having the frequency much higher than the order parameter relaxation rate. Estimations show such an anomaly to be quite observable in the broadening of Mandelstam-Brillouin components near the phase transition in NH_4Cl.[10]

Defects may induce temperature dependent anomalies for transverse acoustic waves also. These anomalies are due to defect induced coupling between the oscillators ζ (transverse acoustic mode) and η, which is described by the sixth term in eq. (1). Really, in the vicinity of the defect $\partial\eta_e/\partial x_i \neq 0$, so the non-linear coupling relevant for a pure crystal gives rise to linear one for a defect crystal. The temperature dependence of the defect contribution to the damping constant of the transverse acoustic mode is $\Delta\Gamma_\zeta \backsim \tau^{-1/2}$ for the sound frequencies less than the order parameter relaxation rate. This anomaly disappears for the high frequency transverse acoustic waves. The anomalies of the attenuation of the transverse acoustic waves have been observed in Rb_2ZnCl_4.[11] They were mentioned to be different for different samples.

As to the interaction described by the fifth term in eq. (1), when it is possible for a phonon mode of any transformation properties, the interaction may provide only non-linear coupling even in a defect crystal. In fact, in the presence of the defect this term transforms to the third order term $2\tau_2\eta_e\eta'\psi^2$. The temperature anomalies caused by such a coupling are very weak.

In conclusion, let us discuss the defect influence on lattice vibrations having the same transformation properties as the order parameter has. In this case we may add the terms $\tau_4\eta\varphi+\tau_5\eta^3\varphi$ to eq. (1). The defect influence is described only by the term $\tau_5\eta^3\varphi$ which provides the additional linear coupling between η' and φ written in the form $3\tau_s\eta_e^2\eta'\varphi$. However, this coupling leads only to temperature independent renormalization of the constant r_4.

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