Dynamics of a Locally Distorted Impurity in a Host Crystal with Displacive Phase Transition

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Received August 16, 1979

We study the dynamic behaviour of a soft displacive impurity in a host crystal undergoing a displacive phase transition. The impurity-induced localized mode and the dynamic autocorrelation function of the impurity below the local freezing temperature are investigated in mean-field approximation (MFA). Furthermore, we give a physical interpretation of the MFA result of the local freezing-out, and discuss the fluctuation behaviour of various types of impurities in relation to recent experiments.

I. Introduction

Recent calculations of various models [1-4] have shown that an isolated impurity in a host crystal undergoing a structural phase transition (PT) may induce a state of local order around the impurity at temperatures above the bulk critical temperature $T_c$. This behaviour is caused by a condensation of an isolated frequency which is pushed down by the soft optical phonon band of the host crystal.

In Ref. 1, the behaviour of an impurity in a three-dimensional crystal was calculated within the mean-field approximation (MFA), and the conditions for the existence of such a local freezing-out were discussed. Schäfer et al. [2] considered the static and dynamic behaviour of an isolated impurity in a lattice-dynamical spherical model. Schmidt and Schwabl [4] investigated the influence of a defect in a one-dimensional Ginzburg-Landau model.

It is obvious that true local freezing-out as a phase transition indicated by a singularity in the free energy can only occur in systems with infinite-range interaction or in MFA. With respect to real crystals we interpret the above result of the local freezing-out at $T_{c}^{\text{loc}} > T_c$ as the appearance of a local dynamic displacement field the motion of which is characterized by two different time scales. Experimental support of this interpretation is provided by recent measurements of Yacoby [5, 6] and Höchli et al. [7]. Yacoby performed induced second-order Raman scattering experiments, which demonstrate the existence of local regions of distorted phases in Na and Li doped KTaO$_3$, and which measure the frequencies of localized modes in the disordered phase of the host crystal. In addition to these oscillatory modes, Yacoby finds from optical depolarization experiments that these impurity-induced microdistortions are dynamic with a relaxation time which is strongly temperature dependent and essentially 5 decades slower than the usual soft-mode frequencies.

More detailed information concerning this slow impurity relaxation process is obtained from dielectric relaxation measurements by Höchli et al. [7]. In view of these experiments it appears very desirable to have theoretical calculations of the dynamic behaviour of a defect also below the local freezing temperature. We therefore extend the previous calculations of Ref. 1, which were restricted to the region $T > T_{c}^{\text{loc}}$, to give a better understanding of the impurity dynamics and to include the dynamics below the local freezing temperature $T_{c}^{\text{loc}}$.

In Sect. II we briefly summarize the properties and the mean-field approach to the model. In Sect. III we discuss the static properties below the local freezing temperature $T_{c}^{\text{loc}}$. The behaviour of the localized mode is investigated in Sect. IV. Section V is devoted to the calculation of the dynamic autocorrelation function below $T_{c}^{\text{loc}}$ and in Sect. VI finally, we give a
physical interpretation of the local order parameter and discuss the fluctuation behaviour of various types of impurities in relation to recent experiments.

II. Model and Mean-Field Approach

We give here a short summary of the mean-field treatment of the system. For details the reader is referred to Ref. 1. We consider a system described by a one-dimensional ferrodistortive order parameter. The model Hamiltonian is given by

$$\mathcal{H} = \sum_{i=1}^{N} \left( \frac{P_i^2}{2M} + V(Q_i) \right) - \frac{1}{2} \sum_{i=1}^{N} \frac{1}{v_{ii}} Q_i Q_i' + \Delta \mathcal{H}_{\text{pert}}(P, Q),$$  

where the $Q_i$ are the local normal coordinates of the soft optical phonon branch and the $P_i$ are the conjugate momenta. We use the usual quartic single-particle potential

$$V(Q_i) = \frac{1}{2} \kappa Q_i^2 + \frac{1}{2} \gamma Q_i^4 \quad (i \neq i).$$  

The displacive impurity at lattice site $i = i$ is described by a single-particle Hamiltonian

$$\mathcal{H}_{\text{imp}}(P_i, Q_i) = \frac{P_i^2}{2M} + V(Q_i) = \frac{P_i^2}{2M} + \frac{1}{2} \kappa Q_i^2 + \frac{1}{4} \gamma Q_i^4.$$  

For simplicity, we disregard any change of the bilinear interactions $v_{ii}$ by the impurity.

The local thermodynamic properties of the perturbed system are calculated in MFA [1, 3]. We use the impurity coordinate $Q_i$ itself as local order parameter and look for a locally ordered state $Q_i \neq 0$. The displacement field $\langle Q_i \rangle$ in the neighbourhood of the impurity is for $T < T_c < T_c^\text{loc}$ approximately given by

$$\langle Q_i \rangle = \frac{\chi_i(T)}{\chi_{ii}(T)} \langle Q_i \rangle_i,$$

in terms of the static susceptibility matrix $\chi_{ii}(T)$ of the host crystal. The difference of the free energies of the locally ordered $\langle Q_i \rangle_i \neq 0$ and the disordered $\langle Q_i \rangle_i = 0$ phase may be written [8]

$$\Delta F = -\frac{1}{2} \lambda(T) \langle Q_i \rangle_i^2 + \tilde{\mathcal{F}}(\langle Q_i \rangle_i) - \tilde{\mathcal{F}}(\langle Q_i \rangle_i = 0),$$

where $\lambda(T)$ is a feedback factor giving the strength of the mean field at the impurity site,

$$F_{\text{pert}}^m = \sum_i v_{ii} \langle Q_i \rangle_i = \lambda(T) \langle Q_i \rangle_i,$$

$$\lambda(T) = \sum_i v_{ii} \chi_i(T) / \chi_{ii}(T) \equiv \chi_{ii}^{-1}(T) - \chi_{ii}^{-1}(T),$$

with $\chi_i(T)$ being the single-particle susceptibility of the host.

The perturbed single-particle free energy is given by [8, 10]

$$\mathcal{F}_2(\langle Q_i \rangle_i) = \frac{1}{2} \left( \kappa + 3 \gamma \hat{\delta} \right) \langle Q_i \rangle_i^2 + \frac{1}{4} \gamma \langle Q_i \rangle_i^4 + \frac{1}{2} \kappa \hat{\delta} + \frac{1}{2} \gamma \hat{\delta}^2 - \frac{1}{2} kT \log \hat{\delta},$$

where the mean-square fluctuation $\hat{\delta} = \langle Q_i^2 \rangle_i - \langle Q_i \rangle_i^2$ has to be determined self-consistently from

$$\hat{\delta} = kT \hat{\chi}_i(T) = kT \bar{M} \hat{\Omega}_i^2(T),$$

$$\hat{\Omega}_i^2(T) = \kappa + 3 \gamma (\hat{\delta} + \langle Q_i \rangle_i^2).$$

The equation of state $\langle Q_i \rangle_i = f(T)$ is found by minimizing $\Delta \mathcal{F}$ which yields

$$\langle Q_i \rangle_i (\kappa + 3 \gamma \hat{\delta} + \gamma \langle Q_i \rangle_i^2) = \lambda(T) \langle Q_i \rangle_i = f^m_i.$$  

By eliminating $\langle Q_i \rangle_i$ and $\hat{\delta}$ from (9a, b) and (10) one obtains for the effective Einstein frequency $\hat{\Omega}_i(T)$ of the impurity the equation

$$\hat{\Omega}_i^2(T) = \left( \frac{3}{2} \lambda(T) - \kappa \right) + \sqrt{\left( \frac{3}{2} \lambda(T) - \kappa \right)^2 - 6 \gamma kT}.$$  

The local dynamic properties follow from the dynamic susceptibility of the impurity ion which is given by

$$\hat{\chi}_{ii}^{-1}(T, \omega) = \chi_{ii}^{-1}(T, \omega) - \mu(T, \omega),$$

where $\mu(T, \omega)$ is the local enhancement factor determined by

$$\mu(T, \omega) = \chi_\omega^{-1}(T, \omega) - \chi_{ii}^{-1}(T, \omega).$$

Here, $\chi_{ii}(T, \omega)$ and $\chi_\omega(T, \omega)$ are the dynamic single-particle susceptibilities of the impurity and of a normal ion, respectively,

$$\chi_{ii}^{-1}(T, \omega) = M(\Omega_i^2(T) - \omega^2),$$

$$\chi_\omega^{-1}(T, \omega) = M(\Omega_\omega^2(T) - \omega^2),$$

where $M \Omega_i^2(T)$ is determined by Eq. (9c) and $M \Omega_\omega^2(T)$ is for $T \geq T_c$ given by [1]

$$M \Omega_\omega^2(T) = \frac{1}{2} [\kappa + (\kappa^2 + 127 \gamma kT) \omega^2].$$

The local susceptibility $\chi_{ii}(T, \omega)$ of the host has the form

$$\chi_{ii}(T, \omega) = \sum_q (M(\omega_q^2(T) - \omega^2))^{-1},$$

where

$$M \omega_q^2(T) = M \Omega_q^2(T) - v_q$$

determine the frequencies $\omega_q(T)$ of the soft optical phonon branch of the host, and $v_q$ is the Fourier transform of the interaction $v_{ii'}$. 