Self-Consistent Phonons in Configurationally Disordered Quantum Crystals. I. Theory

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A generalization of the coherent potential approximation (CPA) to strongly anharmonic systems is presented that takes into account the static relaxations in the vicinity of each defect and the changes in the averaged mean lattice constant and in the mean square fluctuations. In the limits of a perturbed classical, harmonic crystal or an ideal, anharmonic crystal the theory reduces to the conventional CPA and the self-consistent phonon results, respectively. For the numerical solution an approximation is used that starts from the renormalized harmonic phonons in ideal crystals. As an example, some characteristic results are discussed for the systems of oD₂ or pH₂ in Ne.

1. INTRODUCTION

The particles in classical crystals oscillate about their mean positions with amplitudes small compared to the particle separation. Their motions are adequately described in terms of harmonic vibrations. Quantum crystals, on the other hand, have oscillation amplitudes that are considerable compared to the lattice spacing, even at low temperatures. Hence an expansion of the potential energy of the crystal in powers of the particle displacements cannot be truncated after quadratic terms. In addition, in helium and molecular hydrogen the phonon frequencies obtained in this approximation would be purely imaginary, which indicates unstable crystals, contrary to reality. Ideal, that is, translationally invariant, quantum crystals can be treated in the self-consistent phonon theory (SCP) (see, e.g., Refs. 1 and 2). In this theory the force on a particle is derived by regarding all other particles as moving equivalently and not as being fixed at their mean lattice sites as in the classical theory. This leads to an effective restoring force given by an average over the first derivative of the potential weighted by the pair distribution function of the particles.³

*Deceased.
In configurationally disordered crystals, however, the translational invariance is destroyed and the SCP is no longer applicable. The first successful self-consistent approximation for the properties of disordered systems was the coherent potential approximation (CPA).\textsuperscript{4,5,16} The CPA is a harmonic single-site approximation for alloys with random disorder. In the CPA the disordered crystal is described by a translationally invariant effective medium that differs from the unperturbed crystal only by a lattice-periodic, complex, coherent potential. This potential is determined so that a defect embedded in the effective medium produces no further scattering.

A substitutional defect in a crystal generally produces several changes: a relaxation of neighboring particles into new equilibrium positions, changes in the mean square fluctuations, as well as changes in the coupling between all particles in a certain vicinity around the defect. In its original form, developed independently by Soven and Taylor,\textsuperscript{5} the CPA does not describe any of these effects. It is valid only for diagonal disorder, for instance, the mass change at the defect sites in phonon systems or the change in the energy levels in the electronic tight-binding model. Off-diagonal disorder, changes in the coupling of the particles, can be taken into account only for independent defects. This means that the spaces around the defects where their neighbors are affected must not overlap. Clearly this is valid only for low defect concentrations. Most attempts to generalize this method to include off-diagonal disorder at higher defect concentrations or to allow cluster scattering led to at least partly unphysical solutions (see Ref. 7 for references). A successful generalization, the so-called cluster-CPA, has been derived by Mookerjee et al.\textsuperscript{6} and Kaplan et al.\textsuperscript{7} within the augmented space formalism introduced by Mookerjee (see Ref. 8 for a description). This method, as well as the CPA, is a harmonic theory and cannot explain the relaxation of the defect neighbors. To include anharmonicities one can try to combine the SCP with the CPA or its generalizations.

The first attempts to use the SCP in solving defect problems were made by Varma\textsuperscript{9} and Zavt and Reifman.\textsuperscript{10} They considered a quantum crystal containing a single isotopic defect. Contrary to the harmonic case, an isotopic defect in an anharmonic crystal also produces a change in the coupling with its neighbors since the particle motions are strongly correlated and influence the effective coupling. This leads to a set of equations for the eigenvectors and eigenfrequencies (resp. the Green's functions) and for the distortion around the defect to be solved self-consistently. Plakida et al.\textsuperscript{11} used the CPA to calculate the dynamics of a ferroelectric described approximately by harmonically coupled atoms in a static double-well potential given by a sum of quadratic and fourth-order terms in the atom positions. The Hamiltonian of this system is approximated by a quasiharmonic operator in a way similar to the renormalized harmonic phonon approach.\textsuperscript{12}