

Local modes, phonons, and mass transport in solid ^4He

N. Gov and E. Polturak

Department of Physics, Technion-Israel Institute of Technology, Haifa 32000, Israel

(Received 30 December 1998)

We propose a model to treat the local motion of atoms in solid ^4He as a local mode. In this model, the solid is assumed to be described by the self-consistent harmonic approximation, combined with an array of local modes. We show that in the bcc phase the atomic local motion is highly directional and correlated, while in the hcp phase there is no such correlation. The correlated motion in the bcc phase leads to a strong hybridization of the local modes with the $T_1(110)$ phonon branch, which becomes much softer than that obtained through a self-consistent harmonic calculation, in agreement with experiment. In addition, we predict a high-energy excitation branch that is important for self-diffusion. Both the hybridization and the presence of a high-energy branch are a consequence of the correlation, and appear only in the bcc phase. We suggest that the local modes can play the role in mass transport usually attributed to point defects (vacancies). Our approach offers a more overall consistent picture than obtained using vacancies as the predominant point defect. In particular, we show that our approach resolves the long-standing controversy regarding the contribution of point defects to the specific heat of solid ^4He . [S0163-1829(99)13425-8]

I. INTRODUCTION

Atomic motion in solid ^4He was extensively studied over the years, both theoretically and experimentally.¹ The quantum nature of the solid comes into play mainly through the large amplitude of zero-point motion of the atoms in the lattice, an effect especially evident in the solid at its lowest density. In this paper, we shall discuss only these low-density solids ($\sim 21 \text{ cm}^3$ molar volume). Calculations of the phonon spectrum within the self-consistent harmonic approximation seem to agree fairly well with experiment in the hcp phase,² while in the bcc phase, only the energy of the $T_1(110)$ phonon is overestimated by a factor of 2.³ Corrections resulting from the local motion of the atoms due to quantum effects are treated using correlated basis wave functions.¹ A problem that so far was not addressed within these models is that of mass transport, arising from atomic exchange at low temperature. At higher temperatures, this exchange is assumed to occur with thermally activated point defects, traditionally taken as vacancies. With point defects, some additional complexity is to be expected, as here one deals with objects of a size similar to that of the zero-point amplitude of the atom. The existence of thermally activated nonphonon excitations is well established experimentally by several different techniques, such as NMR,⁴⁻⁷ mass diffusion,^{8,9} ion mobility,¹⁰ and x-ray diffraction.¹¹ However, the properties of point defects deduced from these various experiments have so far led to controversial conclusions. For example, taking the experimentally determined activation energies at face value, the calculated density of vacancies is so large that their contribution to the specific heat should be comparable to that of the phonons.^{12,8} This is not borne out by the specific-heat data. Several attempts were made to reconcile this controversy by using the assumption that vacancies in solid ^4He are delocalized and occupy an energy band.^{13,12,8} In this approach, the magnitude of the specific heat is divided by the bandwidth, so that it can be made small through the choice of a sufficiently large bandwidth.

However, in order to obtain a realistic magnitude of the specific heat one has to choose an unphysically large bandwidth, so that this approach is unsuccessful in settling the controversy.⁸

In this paper, we propose a somewhat different description of the solid, one that treats the motion of the atom inside its potential well as a "local mode." Local modes as excitations in anharmonic crystals were discussed previously by Takeno and Sievers,¹⁴ and by Flynn and Stoneham.¹⁵ We show below that the other degrees of freedom are largely decoupled from this local motion. As such, these modes can be assumed to be additional degrees of freedom of the solid, three per atom. The excited states of these local modes can be thermally activated, and seem to reproduce all the physical effects usually attributed to vacancies. Moreover, we show that this picture has none of the inconsistencies connected with vacancies. The properties of the local modes are different in the bcc and the hcp solid phases. In the bcc phase, we show that it is energetically advantageous for the local motion of the different atoms to be correlated. The new ground state has several new features, among them a softened transverse phonon mode and a high-energy excitation branch that opens an additional channel for atomic diffusion. In contrast, the triangular symmetry of the hcp lattice frustrates the possibility of long-range ordering of the local modes, which therefore remain uncorrelated. In both phases the local modes are highly directional due to the anisotropic potential seen by an atom in the crystal, a constraint that we show leads to a small contribution to the specific heat of the solid.

II. LOCAL MODES IN bcc ^4He

Calculations of the ground-state energy of bcc ^4He usually employ variational wave functions that account for the short-range correlations between the atoms.¹ Since we want to focus here on the nature of the local motion of the atom inside the lattice, we will take a different approach. In this

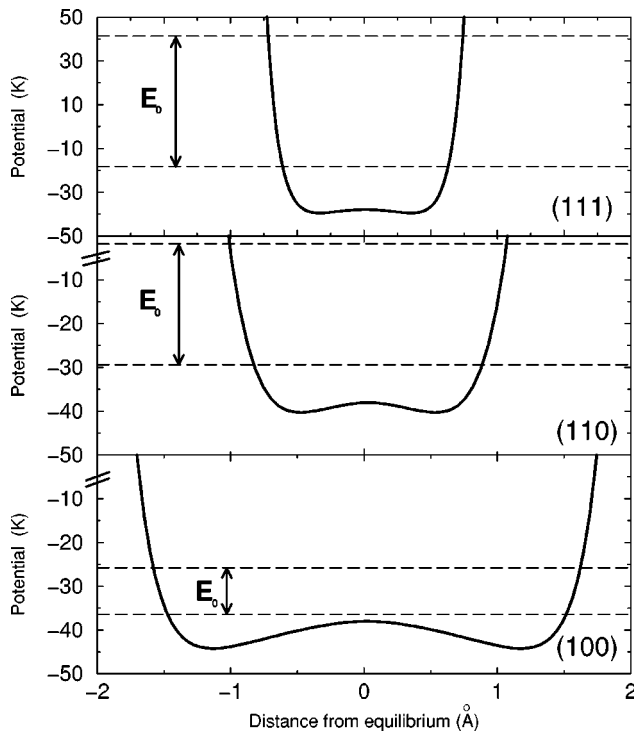


FIG. 1. The potential well of an atom in bcc ^4He along different directions. The energy difference E_0 between the lowest two energy levels (dashed lines) are (111), 59.5 K; (110), 27.6 K; (100), 10.6 K.

approach we would like to isolate the lowest-energy excited state of the atom inside its potential well, and treat it as a local excitation of the lattice. This excited state consists of a local oscillatory motion of the atom along a particular direction and produces an oscillating electric dipole, similar to the usual van der Waals interaction. Unlike in the case of the van der Waals interaction, in which the dipolar fluctuations are random, we show that in the bcc solid these local dipoles are correlated and a new ground state of lower energy is created. We therefore begin by investigating the potential well of an atom in the bcc lattice. This can be done in the following way: Using the standard helium pair potential $v(r)$ (Ref. 1) and taking the atoms as stationary we can map the potential well near an atom along any direction in the lattice. In order to obtain meaningful numerical values, we scaled the potential $v(r)$ so that the calculated one-dimensional potential energy and kinetic energy, averaged over the different directions, reproduce the known kinetic, potential, and total energy of the bcc phase:¹ $\langle E_{kin} \rangle \approx 34$ K, $\langle V \rangle \approx -40$ K, $\langle E_{total} \rangle \approx -6$ K. In Fig. 1 we plot this potential, along the main directions (100), (110), and (111). It is clear that in the directions normal to the cube's faces [i.e., (100), (010), and (001)] the confining potential well is very wide with a pronounced double-minimum structure.

We also plot in Fig. 2 the lowest two energy levels of a one-dimensional Schrödinger's equation for a ^4He atom solved in each of the potential wells. The energy difference between these two levels is lowest in the normal direction, of the order of 10 K. The atomic displacement is described by a mixing between the lowest two energy levels in the potential well, which corresponds to a motion with amplitude of ~ 1 Å (in the normal direction). Although the above treat-

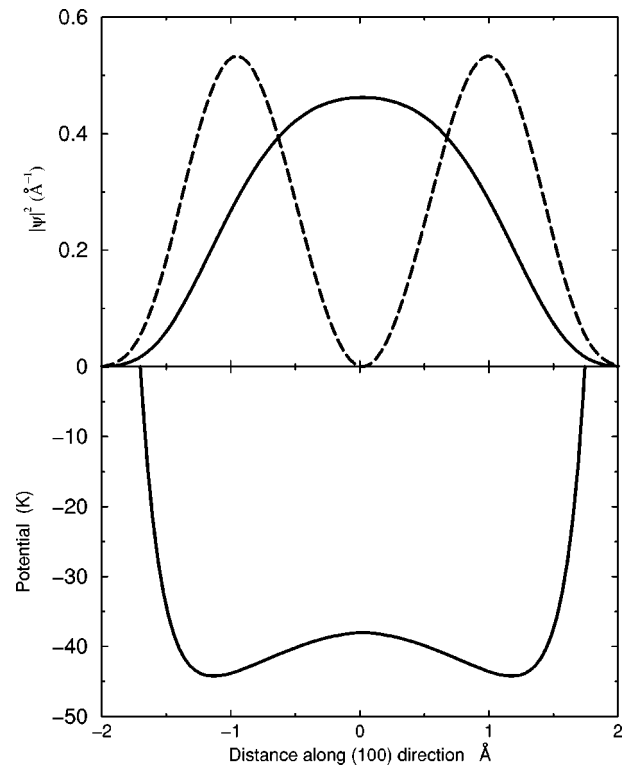


FIG. 2. The probability distribution in the (100) potential well (shown in the lower part). The ground-state wave function is the solid line, while the dashed line is the first excited state.

ment assumes that other atoms are stationary, it indicates the directions along which there will be large amplitude local motion in the solid. It is evident that the motion will be highly directional, with the largest amplitude along the normal direction, while in the other directions the amplitude is much smaller. Allowing other atoms to move as well, so that they get out of each other's way, can only soften the potential well and reduce the value of the energy-level difference, since the potential will effectively become shallower. For example, a calculation that allows opposite atoms to move slightly, reduces the energy difference in the normal direction to almost 6 K.

Based on the above calculation, we shall assume that the atoms have a local mode that is highly directional along one of the directions equivalent to (100), and of energy 6–10 K. Experimental evidence for the existence of such a "local mode" comes from NMR measurements of the linewidth ($1/T_2$) in bcc ^3He - ^4He mixture crystals.⁵ The motional narrowing of the NMR resonance line with temperature shows thermally activated behavior with an activation energy of 7 ± 1 K.^{5,4} At temperatures above 1 K, the NMR line in the solid becomes narrower than that of the liquid, indicating that the atomic motion in the solid is faster than in the liquid. At the same time, the diffusion coefficient of the solid remains several orders of magnitude smaller than that of the liquid,⁵ indicating that this rapid motion is of a local nature. We propose to identify this rapid motion as associated with the excited state of an atom in the well, with an activation energy of $E_0 \approx 7 \pm 1$ K.

A calculation similar to that presented above will give in an harmonic solid the energy of the longitudinal phonon at the edge of the Brillouin zone. In such a calculation one

takes the usual van der Waals interaction, which results from dipolar fluctuations of random direction. The interaction is of second order in the dipolar field ($1/r^6$). In addition, in bcc ^4He we have an excitation of the atoms that involves large and highly directional atomic motion. This highly directional motion of the atom results in the creation of a local (oscillating) electric dipole in the direction of the motion. This local electric dipole is created due to inertia, as the electronic cloud can be thought of as being slightly displaced relative to the ion. We show below that these directional electric dipoles can become perfectly correlated to lower the total energy, and will therefore have first-order and long-range dipolar interactions ($1/r^3$). In an isotropic medium these correlated dipoles cannot arise and there is only the isotropic van der Waals interactions, while here we find the additional dipolar interactions. The three orthogonal dipole moments per atom, which arise from the relative displacement of the nucleus and the electronic cloud, introduce three new degrees of freedom per atom.

The electric dipole due to mixing of the $|s\rangle$ and $|p\rangle$ electronic levels of the ^4He atom. The amount of mixing can be estimated from perturbation theory¹⁶ as

$$\begin{aligned} \psi &= |s\rangle + \lambda |p\rangle \Rightarrow E_0 = \langle \psi | E | \psi \rangle - \langle s | E | s \rangle = \lambda^2 \langle p | E | p \rangle \Rightarrow \lambda^2 \\ &\approx 7/2.46 \times 10^4 \approx 0.00284, \quad \lambda \approx 0.0168, \end{aligned} \quad (1)$$

where $|s\rangle$ and $|p\rangle$ stand for the ground state and first excited state of the ^4He atom, E stands for the nonperturbed atomic energy, λ is the mixing coefficient and $\langle p | E | p \rangle \approx 2.46 \times 10^4$ K is the excitation energy of the first atomic excited state.¹⁷ The estimated mixing is small and the magnitude of the induced dipole moment is therefore

$$|\mu| = e \langle \psi | x | \psi \rangle \approx 2e\lambda \langle s | x | p \rangle \approx e \times 0.03 \text{ \AA}, \quad (2)$$

where $\langle s | x | p \rangle \approx 0.9 \text{ \AA}$. The estimation of the mixing λ and the dipole moment $|\mu|$ serves to set an upper bound on the magnitude of this effect. Since the atoms possess an oscillatory electric-dipole moment they have long-range dipole-dipole interactions.

It is possible to show that the lowest energy of a correlated dipolar array in the bcc lattice preserves the symmetry of the bcc unit cell along one of the symmetry axes. In such a case it can be easily shown that there will be no contribution to the dipolar interaction energy from dipole moments that are orthogonal, and the instantaneous dipolar interaction energy for each of the three orthogonal directions, is given by

$$E_{dipole} = -|\mu|^2 \sum_{i \neq 0} \left[\frac{3 \cos^2[\mu \cdot (\mathbf{r}_0 - \mathbf{r}_i)] - 1}{|\mathbf{r}_0 - \mathbf{r}_i|^3} \right], \quad (3)$$

where the sum is over all the atoms in the lattice, \mathbf{r}_i being the instantaneous coordinate of the i th atom. For oscillating dipoles with random phases, the average instantaneous interaction energy summed over the lattice would be zero. However, the energy of a dipolar array can be made lower by correlating the phases of the oscillating atoms. The lowest interaction energy arrangement of the dipoles in the bcc lattice is such that they are oscillating with the same phase. Since the direction of the dipole shows the instantaneous direction of the motion or displacement, such a state is just a

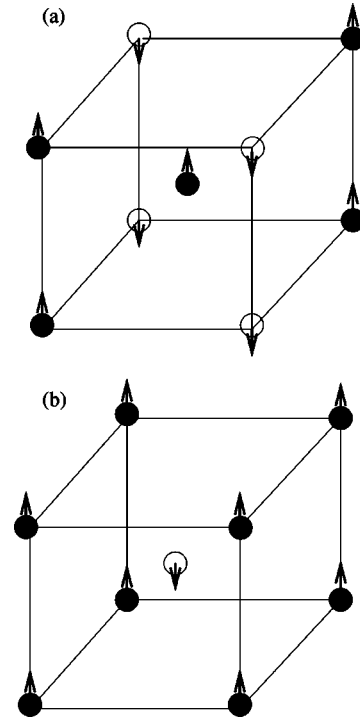


FIG. 3. The two ‘‘antiferroelectric’’ arrangements of the dipoles lying along the major axes of the bcc phase. The atoms having the same dipole moments have the same shade. The sum of the dipole-dipole interaction [Eq. (3)] for a unit dipole moment are (a) -0.08 , (b) $0.0 \text{ (\AA}^{-3}\text{)}$.

uniform motion or translation of the entire lattice. This arrangement is therefore unphysical, and we have to look for symmetric arrangements with respect to the number of up/down dipoles. The two ‘‘antiferroelectric’’ configurations along the symmetry axes of the crystal with individual dipoles oriented along the (001) direction, and a zero total dipole moment. For these two physical possibilities the sum in Eq. (3) with a unit dipole is given in Fig. 3. Thus, the ground state in our picture has the atoms executing this local oscillation in a correlated fashion, as shown in Fig. 3(a) along one particular direction. Independently, similar correlated motion exists in the other two orthogonal directions [i.e., (100) and (010)].

III. ELEMENTARY EXCITATIONS OF THE DIPOLE GROUND STATE

The ground state of the dipoles described in the preceding section will be affected by the excitations of the lattice, namely phonons. In fact, our basic assumption in which the local motion can be separated from these other degrees of freedom needs justification. The oscillatory atomic motion induced by the phonons will modulate the relative phases of the dipoles. Let us look at the ground state of the dipoles, concentrating for example on oscillations oriented along the (001) direction. We now need to consider only phonons that will modulate the local motion along this direction. In the bcc structure, only three phonons fulfill this condition: $L(001)$, $T(100)$, and $T_1(110)$. Let us calculate the energy of the dipolar array when modulated along these three directions. For a modulation along some direction \mathbf{k} , the dipolar

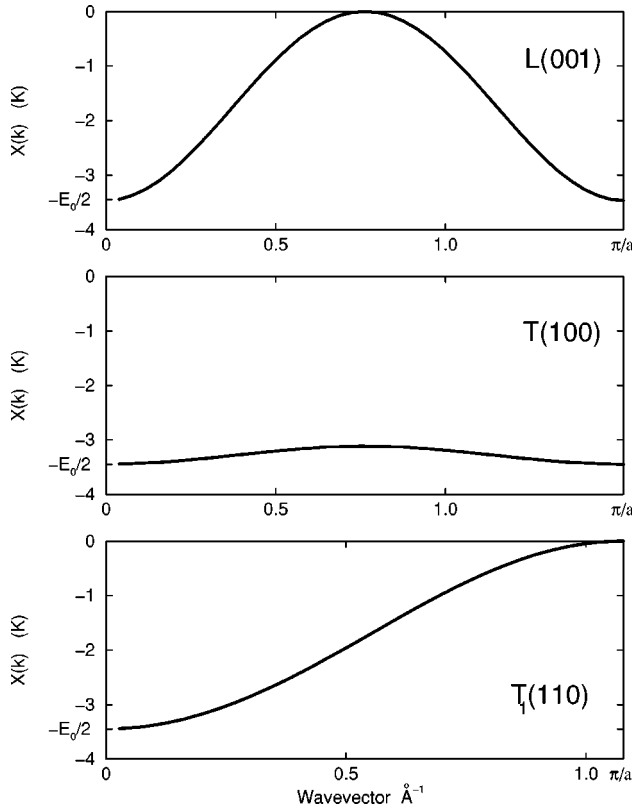


FIG. 4. The calculated interaction matrix $X(k)$ [Eq. (4)] as a function of the wave vector k , for the three phonon modes that could affect a dipolar array. The dipole moment has been normalized to give a gapless mode: $X(k=0) = -E_0/2$. The unit-cell dimensions (\AA): $a = 4.12/2$, $a' = a\sqrt{2}$.

interaction energy is given by¹⁸

$$X(\mathbf{k}) = -|\mu|^2 \sum_{i \neq 0} \left[\frac{3 \cos^2[\mu \cdot (\mathbf{r}_0 - \mathbf{r}_i)] - 1}{|\mathbf{r}_0 - \mathbf{r}_i|^3} \right] \times \exp[2\pi i \mathbf{k} \cdot (\mathbf{r}_0 - \mathbf{r}_i)]. \quad (4)$$

At $k=0$ the interaction matrix $X(k)$ is just the dipolar energy (3).

In Fig. 4 we plot the value of $X(k)$, the energy of the dipolar array modulated by the relevant phonons: $L(001)$, $T(100)$, and $T_1(110)$. We see that for a modulation by $L(001)$ and $T(100)$ the periodicity of $X(k)$ is over a full unit cell that is twice the periodicity of these phonons. Since symmetric functions of periodicities π/a and $2\pi/a$ are orthogonal, the wave functions of the phonons and of the dipole excitations are orthogonal along these directions. The dipole array cannot therefore be excited by any phonon along these two directions. Regarding the modulation by the $T_1(110)$ mode, here the periodicity of $X(k)$ is the same as that of the $T_1(110)$ phonon, which can therefore couple to the dipole array. We conclude therefore that the coupling of the local modes to the lattice excitations is limited to a single phonon mode, justifying our assumption that the local modes can be treated separately to a good approximation. Thus, the only elementary excitations of the dipole array would be in the (110) direction, in the form of the $T_1(110)$ phonon. We shall

now calculate the dispersion relation of such an excitation by a mean-field solution of an effective Hamiltonian.

The Hamiltonian treatment of interacting local excitations was developed originally by Hopfield¹⁹ for the problem of excitons in a dielectric material. The local excitations are treated as bosons and the effective Hamiltonian describing their behavior is²⁰

$$H_{loc} = \sum_k [E_0 + X(k)] \left(b_k^\dagger b_k + \frac{1}{2} \right) + \sum_k X(k) (b_k^\dagger b_{-k}^\dagger + b_k b_{-k}), \quad (5)$$

where b_k^\dagger, b_k are creation/annihilation operators of the local mode, and $X(k)$ is the interaction matrix element given above Eq. (4). The Hamiltonian H_{loc} (5) that describes the effective interaction between localized modes can be diagonalized using the Bogoliubov transformation $\beta_k = u(k)b_k + v(k)b_{-k}^\dagger$. The two functions $u(k)$ and $v(k)$ are given by

$$u^2(k) = \frac{1}{2} \left(\frac{E_0 + X(k)}{E(k)} + 1 \right), \quad v^2(k) = \frac{1}{2} \left(\frac{E_0 + X(k)}{E(k)} - 1 \right), \quad (6)$$

where $E(k)$, the energy spectrum of the diagonalized Hamiltonian is

$$E(k) = \sqrt{E_0[E_0 + 2X(k)]}. \quad (7)$$

The ground-state wave function of the local modes is given by²¹

$$|\Psi_0\rangle = \prod_k \exp\left(\frac{v_k}{u_k} b_k^\dagger b_{-k}^\dagger\right) |\text{vac}\rangle. \quad (8)$$

We show in Fig. 4 $X(k)$ in the (110) direction using a dipole moment $|\mu|$ determined as follows: we would like, according to our definition of the local mode, that the energy cost of flipping the direction on a single dipole out of the ground state be E_0 . This condition is equivalent to demanding that $2|X(k=0)| = E_0$. We also see from Eq. (7) that in order for the dipoles to have a gapless mode at $k \rightarrow 0$ we must have $X(k=0) = -E_0/2$. Using this condition, the value of $E_0 = 7$ K (see previous section) determines the size of the dipole moment as: $|\mu| \approx e \times 0.01$ \AA . This value is indeed smaller than our previous estimation, which was an upper bound on the size of dipole moment (2).

From its very definition, the phase modulation in the (110) direction of the atomic motion with energy $E(k)$ [Eq. (7)] should be just the $T_1(110)$ phonon. In Fig. 5 we compare the experimental values of $T_1(110)$ taken from the neutron scattering with the calculated $E(k)$. The agreement is excellent for all k . From Eq. (7) and Fig. 4 we find that at the edge of the Brillouin zone the energy $E(k)$ of the phonon is just the bare energy of the local mode, E_0 , since $X(\sqrt{2}\pi/a) = 0$ and the dipoles have changed from the configuration of Fig. 3(a) to Fig. 3(b). We recall that the value of E_0 that we used was taken from NMR data. The agreement between these two independent determinations of E_0 , that from NMR and that from neutron scattering, emphasizes the self-consistency of our description. We stress that the value of E_0 is the only

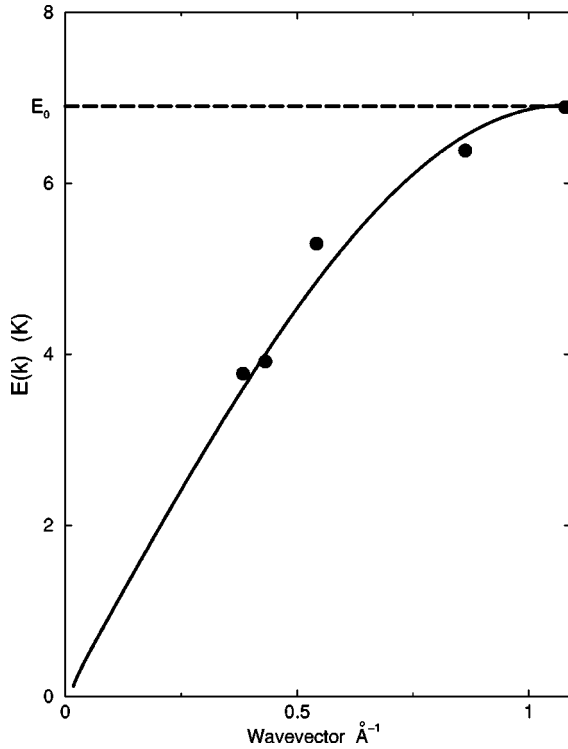


FIG. 5. The experimental data (Ref. 3) (solid circles) for the $T_1(110)$ phonon compared with the calculation [Eq. (7)] (solid line). Also shown is the energy of the bare local mode $E_0 = 7$ K.

empirical input into the calculation, while the functional behavior is completely defined by the lattice structure and the dipolar form of the interactions.

Our model indicates that only the $T_1(110)$ phonon would be different than that obtained from the self-consistent harmonic (SCH) calculation, because it is the only excitation that couples to the local motion. Indeed, in the experiment³ this is the only phonon branch that is not described well by the SCH calculation. The fact that the SCH calculation works rather well for other directions is consistent with our picture in which there are no elementary excitations of the dipole array in these directions.

IV. HARMONIC AND LOCAL-MODE HYBRIDIZATION

An equivalent way to describe the mutual influence between the local modes and the lattice can be done by taking the interaction between the dipoles as resulting from an exchange of virtual harmonic transverse fluctuations of the lattice. An analogous case, that of excitons in a dielectric, was treated by Hopfield¹⁹ (in that case, the interaction is mediated through the exchange of virtual photons). The two excitations, the local mode and virtual harmonic phonon, are then hybridized through the same dipolar interaction matrix $X(k)$, which we used in the direct interaction picture. In our case, the natural choice for the mediating virtual phonon is the $T_1(110)$ phonon, as calculated by the SCH method. The use of the phonon calculated by the SCH method is important, since this calculation is largely independent of the local degrees of freedom described by the local mode. The motivation for using this approach is that it allows us to obtain an additional branch of the excitation spectrum that has observable consequences.

The Hamiltonian describing the local-mode and SCH-phonon hybridization is¹⁹

$$H = H_0 + H_{loc}^0 + H_c, \quad (9)$$

where the three components of Eq. (9) are the SCH phonon

$$H_0 = \sum_k \varepsilon(k) a_k^\dagger a_k, \quad (10)$$

where a are Bose operators and $\varepsilon(k)$ is the SCH-phonon spectrum, and the local mode

$$H_{loc}^0 = \sum_k E_0 b_k^\dagger b_k. \quad (11)$$

The part describing the first-order (dipolar) coupling between the phonons and the localized modes is¹⁹

$$H_c = \sum_k [\lambda(k) b_k + \mu(k) a_k] (a_k^\dagger + a_{-k}) - [\lambda(k) b_k^\dagger - \mu(k) a_k^\dagger] (a_k + a_{-k}^\dagger), \quad (12)$$

where, in the dipolar approximation (and a cubic lattice) the two functions λ and μ are given by $\lambda(k) = iE_0 \{-3X(k)/2\varepsilon(k)^{1/2}\}$ and $\mu(k) = -E_0 3X(k)/2\varepsilon(k)$, with $X(k)$ the dipole matrix element (4). This is just the standard coupling Hamiltonian of an atom to a transverse photon field, which is replaced here by the $T_1(110)$ SCH phonon. The total Hamiltonian H does not involve quartic terms and can be diagonalized using the canonical transformation¹⁹

$$\begin{aligned} \alpha_1 &= A a_k + B b_k + C a_{-k}^\dagger + D b_{-k}^\dagger, \\ \alpha_2 &= B a_k + A b_k + D a_{-k}^\dagger + C b_{-k}^\dagger, \end{aligned} \quad (13)$$

where these operators describe the two branches of the hybridized energy spectrum. The transformation functions $A(k), B(k), C(k), D(k)$ can be written down explicitly.¹⁹ The corresponding dispersion relation is

$$\frac{\varepsilon^2(k)}{E^2(k)} = 1 - \frac{6}{E_0} \frac{X(k)}{1 - \left(\frac{E(k)}{E_0}\right)^2}, \quad (14)$$

which describes two energy branches E_1 and E_2 . The equivalence of this and the treatment in the previous section is due to the use of the same dipole interaction matrix $X(k)$ in both. With $X(k)$, we can solve Eq. (14) to find the two energy branches:

$$\begin{aligned} E_1 &= \varepsilon(k)/2, \\ E_2 &= 2E_0. \end{aligned} \quad (15)$$

We see that the energy of the lower branch E_1 is half of that of the SCH phonon for all k . Comparing the SCH calculation and the experimental results for the $T_1(110)$ phonon, we find that there is indeed a constant, k -independent ratio between them. This ratio turns out to be ~ 1.7 for all momenta, close to the predicted ratio of 2 (15) (Fig. 6). This small discrepancy is within the uncertainty of the SCH calculations and the experimental data. Despite this small dis-

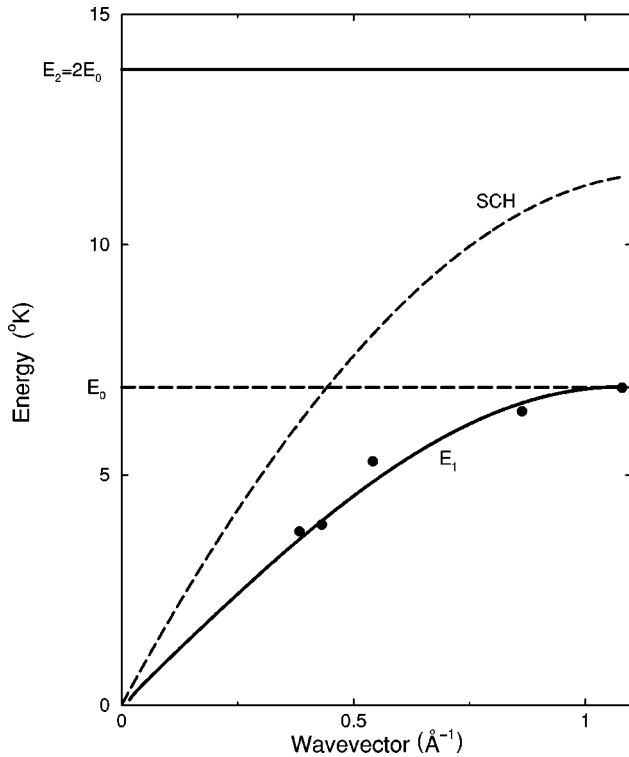


FIG. 6. The SCH calculation (Ref. 1) (dashed line) compared with the experimental results (Ref. 3) (solid circles) for the $T_1(110)$ phonon. Solid line is our calculated spectrum [Eq. (7)]. Also shown is the prediction of the hybridization model [Eq. (15)] for the high-energy branch $E_2 = 2E_0$.

crepancy we find the agreement very satisfying. Our picture of a hybridization of a dipole array with the harmonic lattice can therefore account for the main effect of the local motion. The upper branch E_2 , a dispersionless excitation with energy of 14 K (Fig. 6), was possibly observed in an inelastic neutron-scattering experiment,²² in which a strong feature was observed at an energy transfer of 1.4 meV. This feature was interpreted by Glyde¹ in terms of an interference effect between phonon modes, which is not inconsistent with our hybridization picture. Another possible way to observe this excitation would be by Raman scattering. In addition, this energy branch is important in the process of mass diffusion, and will be discussed in this context in a following section.

We would like to point out that local modes can arise also in classical crystals, as a result of a large anharmonicity.¹⁴ As shown by these authors, these local modes can assume many of the roles of vacancies. There are several similarities between this work and ours: first, the treatment in nonperturbative; second, in a simple cubic lattice, they also find that there are two excitation branches. These similarities occur despite the different basic assumptions of the classical model and the present work, which uses the quantum properties of the crystal as the starting point.

V. LOCAL MODES IN hcp ^4He

We now turn to discuss the effects arising from the local motion in the hcp structure. Repeating the calculation done in Sec. II, we plot in Fig. 7 the potential well along the main directions of the hcp crystal, namely, (1000), (0100), and

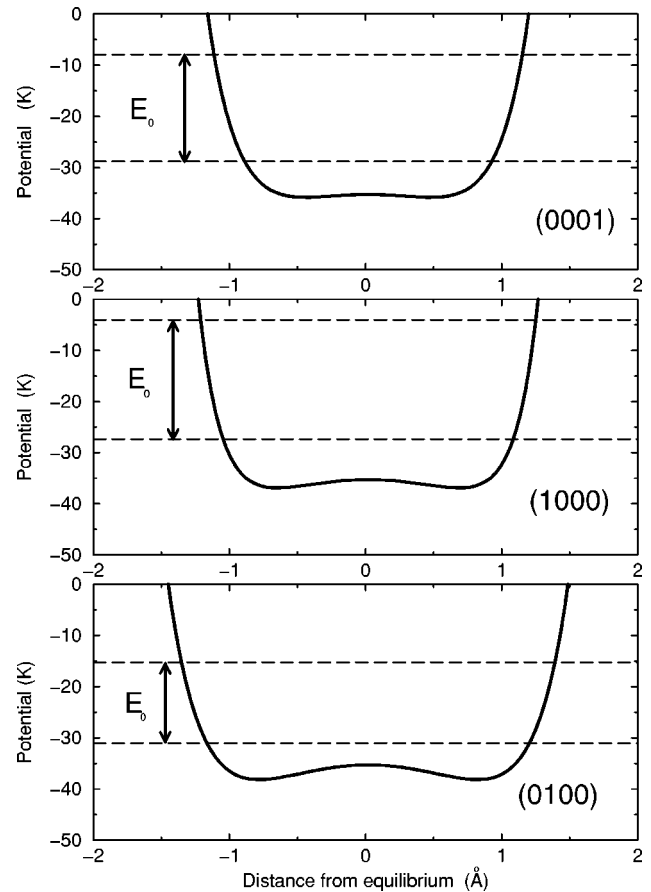


FIG. 7. The potential well of an atom in hcp ^4He along different directions. The energy difference E_0 between the lowest two energy levels (dashed lines) are (0100), 16.0 K; (1000), 21.0 K; (0001), 23.0 K.

(0001). We also plot in Fig. 7 the lowest two energy levels of a one-dimensional Schrödinger's equation solved in each of the potential wells. The energy difference between these two levels is lowest in the (0100) direction, of the order of 16 K. Similar to what was stated for the bcc structure, the calculation indicates the direction along which there will be large amplitude local motion.

As in the bcc phase, evidence for the existence of a “local mode” comes from NMR measurements^{6,23} of the linewidth ($1/T_2$) with energy ≈ 14 K. We propose therefore that the NMR experiments measure the energy of the bare local mode.

In contrast to the bcc phase, we do not expect the local electric dipoles in the hcp phase to have long-range order. This is due to the fact that there is geometric frustration against an “antiferroelectric” order in a triangular lattice. We calculated the dipolar interaction energy for several simple dipole arrangements preserving the net zero dipole moment, and did not find any arrangement in which this energy was negative. Comparison of the SCH calculation of the phonons spectrum with experiment reveals that there is an overall good agreement, with no exceptions, such as found for the $T_1(110)$ phonon in the bcc phase. Thus, we conclude that there is no long-range order within the dipole array like in the bcc phase, and the local modes in the hcp solid are largely uncorrelated.

VI. ATOMIC SELF-DIFFUSION

We have seen that in the first excited state of the atom in its potential well, the atom oscillates with a comparatively large amplitude ($\sim 1 \text{ \AA}$). This motion can have an effect on the atomic exchange rate that is governed by the overlap of the wave functions of neighboring atoms. At low temperature, the atomic exchange, or self diffusion, occurs by tunneling and is small ($D_0 \sim 10^{-9} \text{ cm}^2/\text{s}$ in the hcp phase⁸). Thermally activated diffusion is traditionally attributed to vacancies. We would like to show that thermally excited local modes can produce self-diffusion at rates that compare favorably with experimental data.

The theoretical calculation of the zero-temperature exchange rate of atoms in solid helium is a long-standing problem.²⁴ It is extremely difficult to perform accurate theoretical calculations of this effect due to the smallness of the exchange frequency as compared with the Debye frequency. In these calculations, the atoms participating in the exchange are treated as tunneling along a one-dimensional closed path. At high densities, it is found that the effective potential barrier for tunneling is mainly due to the potential energy associated with the elastic deformation of the crystal during the atomic exchange. At lower densities it is more difficult to calculate the height of the tunneling barrier, but empirically it turns out to be of the order of the kinetic energy of the atoms (30 K–40 K). Thus, in order to obtain a rough estimate of the exchange rate, it is sufficient to view the problem as that of a one-dimensional tunneling of free particles through a square barrier. Since we are dealing with low-density solids, the height of the barrier should be comparable with the kinetic energy of the atoms. We would like to compare the exchange rate of atoms in the ground state with that of atoms in the excited state of the local mode.

We begin with the hcp phase, looking at the (0100) direction, that of the largest amplitude atomic motion. We take the atom in the ground state with its kinetic zero-point energy ($E_{kin} \approx 10 \text{ K}$) and adjust the barrier height to reproduce the experimental rate of exchange at low temperatures. We take the width of the barrier to be $a = 3.6 \text{ \AA}$, i.e., the nearest-neighbor distance. We find that a barrier height of 44 K gives a transmission probability $\Gamma \approx 10^{-7}$, and a self-diffusion coefficient $D_0^G \approx (E_{kin}/\hbar)a^2\Gamma \sim 10^{-9} \text{ cm}^2/\text{s}$, which is consistent with the experimental results. The barrier height found in this estimation is consistent with the empirical value, of the order of the total kinetic energy of the atoms in the solid. We now turn to thermally activated self-diffusion. In the first excited state of atoms in the well, the total energy of the atom is 24 K (10 K from the ground state + 14 K for the first excited level of the local mode). The barrier height remains unchanged, but the atom can now tunnel from one of the lobes of the excited-state wave function (see Fig. 2), which are approximately 1 \AA from its equilibrium position. Since it tunnels into an identical excited state, the effective width of the barrier is now $a = 3.6 - 2 = 1.6 \text{ \AA}$. We thus find a transmission probability in the excited state $\Gamma \approx 10^{-2}$, and a prefactor of the diffusion coefficient $D_0^E \approx (E_{kin}/\hbar)a^2\Gamma \sim 10^{-4} \text{ cm}^2/\text{s}$. This means in our model that as atoms are thermally excited out of the ground state, the diffusion coefficient would increase exponentially with temperature as $D_0^E \exp(-E_0/kT)$. The experimental values⁸ are $D_0^E \approx 10^{-4} \text{ cm}^2/\text{s}$,

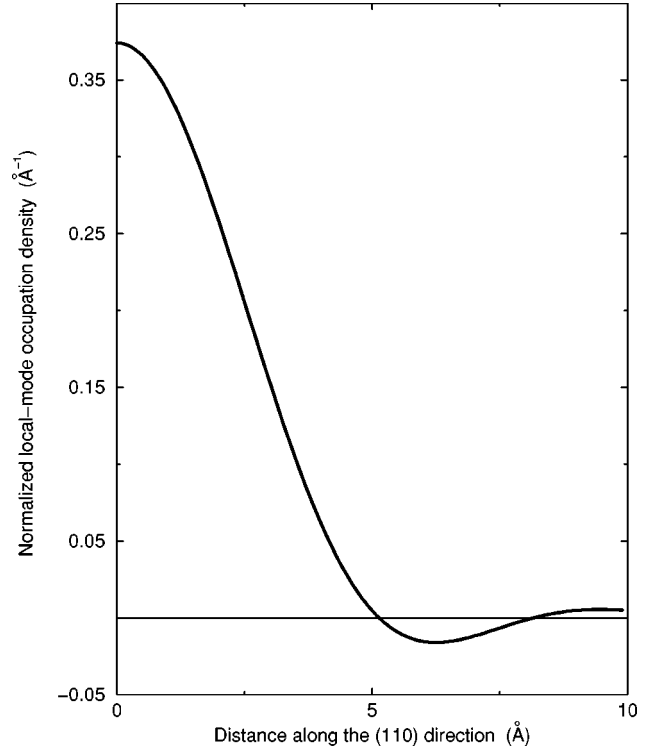


FIG. 8. The normalized Fourier transform of the k -space density of the local-mode occupation in the high-energy branch E_2 [Eq. (16)], along the (110) direction.

and that of the activation energy $E_0 = 13.9 \text{ K}$, which is very close to the value of $E_0 = 14 \text{ K}$ that we took from NMR as describing the energy of the local mode. We therefore conclude that exchange of atoms occupying a thermally activated local mode can account for self-diffusion at a rate usually attributed to vacancies in the hcp phase.

The rate of self-diffusion in the bcc phase is an order of magnitude larger than in the hcp phase.⁸ In this phase, the direction of largest local atomic motion is (100). Repeating the above calculation of the tunneling rate for this case, we have the ground-state kinetic zero-point energy similar to the hcp ($E_{kin} \approx 10 \text{ K}$), and barrier width along the (100) direction of $a = 4.12 \text{ \AA}$. For a tunneling rate at low temperatures that would be higher by an order of magnitude compared with the hcp phase we need a barrier height of $\sim 30 \text{ K}$, which is again close to the total kinetic energy of the atom in the ground state ($\sim 34 \text{ K}$).¹ In order to look at thermally activated self-diffusion, the model used above for the hcp phase is inapplicable, since the energy of the excited state $E_2 = 2E_0 \approx 14 \text{ K}$ (15) is associated with more than one atom. In order to understand the physical nature of this excitation we plot $n_b(r)$ (Fig. 8), the spatial extent of the density of atoms excited by this branch of the local modes in the (110) direction. This is the Fourier transform of the k -space density of the localized modes in the upper branch (13):

$$n_b(k) = \langle b_k^\dagger b_k \rangle_2 = |C(k)|^2. \quad (16)$$

What is seen in Fig. 8 is that the function $n_b(r)$ extends over two unit cells in real space, in the (110) direction. Since the energy is twice the energy of the bare local mode, it can be interpreted qualitatively as two atoms excited in adjacent

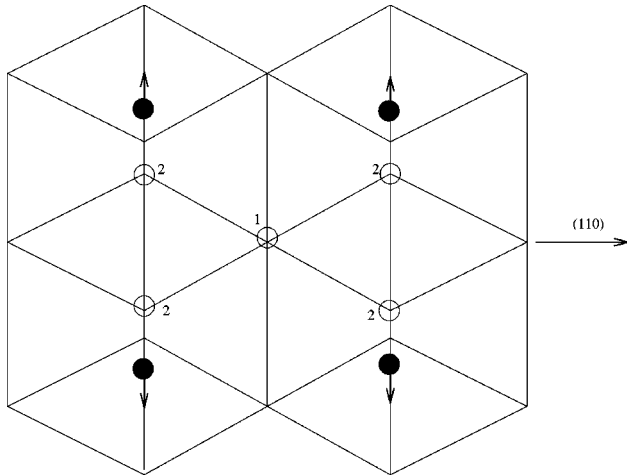


FIG. 9. Schematic picture of an excitation of the high-energy branch $2E_0$, as two adjacent local modes along the (110) direction. The filled circles represent atoms that execute the breathing motion, allowing atoms 1 and 2 (open circles) to exchange places more easily.

unit cells, each having an energy $E_0 = 7$ K. This corresponds to a “flip” of the dipole moment of these two atoms. In Fig. 9 we show that with this excitation, there are four atoms oscillating in such a way, as to reduce the potential barrier for the exchange of atoms 1 and 2. This type of atomic exchange resembles phonon-assisted tunneling, where the correlated “breathing” motion of the four atoms is locally equivalent to a phonon excitation at the edge of the Brillouin zone. This type of self-diffusion was considered in the past,¹⁵ and was recently found to be consistent with experiment in bcc ^4He (Ref. 9) as the dominant mass-transport channel, with an activation energy of 14.8 K.^{8,9} Thus, although quantitative calculations of the rate of diffusion are outside the scope of this paper, both the mechanism and the activation energy are in accord with experiment.

VII. CONTRIBUTION OF LOCAL MODES TO THE SPECIFIC HEAT

One of the controversial issues with vacancies in solid ^4He is that based on the measured values of the activation energy, their estimated contribution to the specific heat is comparable to that of the phonons.^{12,8} Yet, the experimental evidence shows a much reduced contribution.²⁵ Let us consider the contribution of the local modes presented here to the specific heat.

In the bcc lattice we found that the bare local mode with energy $E_0 \approx 7$ K is now changed by the interactions into a phonon and a new localized-mode of twice its bare energy. The nonphonon contribution should therefore be due to the new branch at $E_2 = 2E_0 \sim 14$ K, resulting in a much reduced contribution to the specific heat, in good quantitative agreement with the experimental data, taking the contribution to the specific heat from a two-level system as

$$C_{\text{excess}} = R(E_2/T)^2 \exp(-E_2/T), \quad (17)$$

where R is the ideal gas constant. At $T = 1.6$ K this gives $C_{\text{excess}} \approx 400$ mJ/mole K, which is close to the estimated excess specific heat⁸ of 450 ± 40 (mJ/mole K).

In the hcp lattice there is no long-range order of the local dipoles so that the local-mode contribution should be calculated using the bare energy $E_0 \approx 7$ K. This should give us a nonphonon contribution similar to that in the bcc phase, but the experimental results⁸ indicate a much lower value. This is due to the energy of the local mode being different in each direction of the lattice; the highest contribution to the specific heat would come from the excitation of local modes along the directions where the excitation energy is lowest (i.e., at E_0). Because of the restricted solid angle in which these modes are active, the fraction of phase space occupied by them would be correspondingly small, and their contribution to the specific heat would be much reduced compared with that obtained previously. In these previous estimations, the point defect was assumed to occupy phase space uniformly, thus yielding a large contribution. To obtain a quantitative estimate of the above effect we calculate the ratio between the contribution to the specific heat from directional local modes and the total experimental specific heat of the hcp²⁶ solid phase. We used the energies calculated above for the excitation energies along the principal directions of the hcp lattice (Fig. 7), and a simple linear interpolation for the excitation energies in the intermediate orientations. The maximum contribution is less than 1% of the total specific heat, in agreement with the experimental results.

VIII. CONCLUSION

In this work we have proposed a new approach to treat the local behavior of ^4He atoms in the bcc and hcp solid phases. We treat the excitations of atoms inside their potential well as local modes. The anisotropy of the potential renders these modes highly directional. Due to the symmetry of the bcc phase we propose that the local mode is hybridized with the harmonic density fluctuations (SCH). The hybridization is described by the dipole-dipole interaction and the spectrum of the hybridized $T_1(110)$ phonon is calculated. An additional excitation branch is identified, and it is this branch that seems to control the anomalously large self-diffusion in the bcc solid. In the hcp phase, the symmetry does not allow for correlations of these local modes. Consequently, there is no hybridization with the phonons, and the thermally activated self-diffusion in this phase is controlled by the energy of the bare local mode.

The directionality of the local modes means that their contribution to the specific heat of the solid is negligible. We therefore demonstrated that the local-mode approach can describe experimental data coming from neutron scattering, NMR, and diffusion experiments within one physical model, while at the same time resolving a long-standing discrepancy concerning the specific-heat contribution of point defects. The physical picture of our proposed local mode is very different from the classical picture of a vacancy. We therefore see no reason to consider point defects in solid ^4He as vacancies, as they can be consistently treated as natural excitations of the solid lattice, without having to physically remove atoms from it.

ACKNOWLEDGMENTS

This work was supported by the Israel Science Foundation and by the Technion VPR fund for the Promotion of Research.

- ¹H. R. Glyde, *Excitations in Liquid and Solid Helium*, Oxford Series on Neutron Scattering in Condensed Matter (Clarendon Press, Oxford, 1994).
- ²V. J. Minkiewicz, T. A. Kitchens, F. P. Lipschultz, R. Nathans, and G. Shirane, *Phys. Rev.* **174**, 267 (1968).
- ³V. J. Minkiewicz, T. A. Kitchens, G. Shirane, and E. B. Osgood, *Phys. Rev. A* **8**, 1513 (1973).
- ⁴A. R. Allen, M. G. Richards, and J. Schratler, *J. Low Temp. Phys.* **47**, 289 (1982).
- ⁵I. Schuster, Y. Swirsky, E. J. Schmidt, E. Polturak, and S. G. Lipson, *Europhys. Lett.* **33**, 623 (1996).
- ⁶D. S. Miyoshi, R. M. Cotts, A. S. Greenberg, and R. C. Richardson, *Phys. Rev. A* **2**, 870 (1970).
- ⁷V. N. Grigor'ev, *Low Temp. Phys.* **23**, 3 (1997).
- ⁸N. E. Dyumin, N. V. Zuev, V. V. Boiko, and V. N. Grigor'ev, *Low Temp. Phys.* **19**, 696 (1993).
- ⁹I. Berent, and E. Polturak, *Phys. Rev. Lett.* **81**, 846 (1998).
- ¹⁰A. J. Dahm, in *Progress in Low Temperature Physics, Vol. X*, edited by D. F. Brewer (North Holland, Amsterdam, 1986), p. 73.
- ¹¹R. O. Simmons, *J. Phys. Chem. Solids* **55**, 895 (1994).
- ¹²C. A. Burns and J. M. Goodkind, *J. Low Temp. Phys.* **95**, 695 (1994).
- ¹³A. F. Andreev, in *Progress in Low Temperature Physics, Vol. VIII*, edited by D. F. Brewer (North-Holland, Amsterdam, 1982).
- ¹⁴S. Takeno and A. J. Sievers, *Solid State Commun.* **11**, 1023 (1988).
- ¹⁵C. P. Flynn and A. M. Stoneham, *Phys. Rev. B* **1**, 3966 (1970).
- ¹⁶C. Cohen-Tannoudji, B. Diu, and F. Laloe, *Quantum Mechanics* (Wiley-Interscience, New York, 1997).
- ¹⁷H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill, New York, 1934).
- ¹⁸W. R. Heller and A. Marcus, *Phys. Rev.* **84**, 809 (1951).
- ¹⁹J. J. Hopfield, *Phys. Rev.* **112**, 1555 (1958).
- ²⁰P. W. Anderson, *Concepts In Solids* (Benjamin, New York, 1963), pp. 132–148.
- ²¹K. Huang, *Statistical Mechanics* (Wiley, New York, 1987).
- ²²E. B. Osgood, V. J. Minkiewicz, T. A. Kitchens, and G. Shirane, *Phys. Rev. A* **5**, 1537 (1972).
- ²³I. Schuster, E. Polturak, Y. Swirsky, E. J. Schmidt, and S. G. Lipson, *J. Low Temp. Phys.* **103**, 159 (1996).
- ²⁴M. Roger, J. H. Hetherington, and J. M. Delrieu, *Rev. Mod. Phys.* **55**, 1 (1983).
- ²⁵J. K. Hoffer, W. R. Gardner, C. G. Waterfield, and N. E. Phillips, *J. Low Temp. Phys.* **23**, 63 (1976).
- ²⁶W. R. Gardner, J. K. Hoffer, and N. E. Phillips, *Phys. Rev. A* **7**, 1029 (1973).