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[17]Intrabulk band gaps have not been reported in the papers dealing with the simple-cubic structure. However, gaps are probably the rule in fcc and bcc, since they appear not only in the work on fcc using the present model (Refs. 13 and 2) but also in work on bcc iron (Ref. 10).

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[21]See, e.g., P. M. Morse, in *Handbook of Physics*, edited by E. U. Condon and H. Odishaw (McGraw-Hill, New York, 1967), Pt. 3, Chap. 7.

[22]These remarks on "dynamic decoupling in the adiabatic sense" are meant to be taken only as a heuristic roughly approximate analogy to the adiabatic (Born-Oppenheimer) approximation separating electronic and nuclear motions in the quantum mechanics of molecular systems [cf. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U. P., Oxford, 1954), Sec. 14]. The quality of the approximation is fairly good for the frequencies, but as in the analogous case in quantum mechanics the true eigenvectors are less well represented by the approximate picture.

[23]Strictly speaking, in the present method of studying surface vibrations by calculating the normal modes of a finite crystalline slab, surface branches hybridize considerably with the bulk branches of most bulk bands through which they pass. The result is disappearance of the surface branch as such, leaving behind a locus of mixed modes through the bulk band. Since in a scattering picture of a semi-infinite crystal such loci of mixed modes would be branches of modes only resonantly localized at the surface, we refer to such loci as pseudosurface branches.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 6 15 SEPTEMBER 1971

Quantum Mobility and Nuclear-Spin-Echo Damping in Impure Crystals

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(Received 11 May 1971)

Dash has attributed the low-temperature loss of configurational entropy in impure crystals to the quantum mobility of the impurities. The resulting specific-heat peaks at $T=\Delta/k_B$ have not yet been observed, probably owing to the extremely small values of the mobility bandwidths Δ. In this paper it is shown that if $\Delta \gg \hbar(D^2g/a^3)^{1/3}$, then the mobility bandwidth can be measured via nuclear-spin-echo-damping experiments carried out at temperatures much larger than Δ/k_B. D is the diffusion coefficient, a is the lattice spacing, and $\vec{g}$ is the magnetic-field gradient (measured in frequency units). The damping factor is shown to have an oscillatory character in this limit as opposed to the usual classical $e^{-Dg^2t^3/12}$ form. Practical limits to the method yield $\Delta/k_B \gtrsim 10^{-5}$ °K as an approximate lower bound on detectable widths.

I. INTRODUCTION

Consider the ground-state wave function of a single impurity atom in an otherwise perfect crystal. Let N_s be the number of equivalent binding sites for the impurity. If the impurity were immobile, then the ground state would be N_s-fold degenerate. Furthermore the ground-state degeneracy of a dilute solid solution of $N \ll N_s$ impurities would be[1]

$$\Gamma \simeq N_s^N/N! \,. \tag{1}$$

This gives rise to a macroscopic ground-state configurational entropy

$$S_c = k_B \ln\Gamma \,, \tag{2}$$

which apparently violates the third law of thermodynamics.

It is possible that the entropy S_c is due to a dynamic metastability. If the true stable ground state implied complete phase separation, then the impurity immobility which prevents true equilibrium from being reached would not represent a third-law violation. Dash[2] has suggested another intriguing possibility: the quantum-mobility hypothesis.

Let $\Phi_{\vec{l}}$ represent the many-body wave function for a single impurity to be bound at the lattice site

$$\vec{l} = l_1\vec{a}_1 + l_2\vec{a}_2 + l_3\vec{a}_3 \ . \tag{3}$$

If the Hamiltonian matrix

$$(\Phi_{\vec{l}_f}, \ H\Phi_{\vec{l}_i}) = h(\vec{l}_f - \vec{l}_i) \tag{4}$$

has nonzero off-diagonal matrix elements between different initial and final binding sites, then the impurity is quantum mobile. The N_s-fold binding degeneracy is split into an energy band[3]

$$E(\vec{k}) = \sum_{\vec{l}} h(\vec{l}) e^{-i\vec{k}\cdot\vec{l}} \ , \tag{5}$$

whose eigenfunctions are the traveling waves

$$\Psi_{\vec{k}} = \frac{1}{N_s^{1/2}} \sum_{\vec{l}} e^{i\vec{k}\cdot\vec{l}} \Psi_{\vec{l}} \ . \tag{6}$$

The third-law loss of configurational entropy of $N \ll N_s$ impurities in a quantum-mobile energy band is well understood.[2] If the width of the energy band is Δ, then one can define a site lifetime[4] τ and a mobility temperature T_0 by

$$\Delta = k_B T_0 = \hbar/\tau \ . \tag{7}$$

The configurational entropy S_c is lost at low temperatures via a specific-heat peak at $T \simeq T_0$.

Mobility specific-heat peaks have not yet been observed in impure crystals, presumably because T_0 is too low a temperature for present-day cryogenic technology. However the loss of configurational entropy due to quantum mobility is potentially useful for improving this technology.[2] It is therefore crucial to measure Δ via experiments carried out at higher temperatures $T \gg T_0$. In a previous paper[5] it was shown that T_0 could be inferred from the anomalous broadening of a Mössbauer line in the impurity nucleus. In this paper it will be shown that T_0 can be inferred from an oscillatory behavior of the impurity nuclear-spin-echo-damping factor. Nuclear-magnetic-resonance methods[6] appear to be capable of measuring quantum-mobility bandwidths as small as $\Delta/k_B \sim 10^{-5}$ °K.

II. SPIN-ECHO-DAMPING FACTOR

Let $m(t) = s_x(t) + is_y(t)$ be the transverse spin of an impurity nucleus moving in an inhomogeneous external magnetic field $\omega(t)$ in the z direction. The equation of motion for the nuclear spin is given by

$$\frac{dm(t)}{dt} = -i\omega(t)m(t) - \frac{1}{T_2} m(t) \ , \tag{8}$$

where all of the relaxation mechanisms (except external magnetic field inhomogeneities) are buried in the relaxation time T_2.

If $\vec{v}(t)$ is the velocity of the impurity and $\vec{g}$ is the external magnetic field gradient, then

$$\omega(t) = \omega_0 + \int_0^t \vec{g}\cdot\vec{v}(t_1)\, dt_1 \ , \tag{9}$$

where ω_0 is the magnetic field felt by the impurity at time zero. Equations (8) and (9) imply that the average transverse spin is given by

$$\langle m(t)\rangle = e^{-i\omega_0 t}\, e^{-t/T_2}\, G(t)\, m(0) \ , \tag{10}$$

where

$$G(t) = \langle \exp -i \int_0^t dt_2 \int_0^{t_2} dt_1 \ \vec{g}\cdot\vec{v}(t_1)\rangle \tag{11}$$

is the damping factor due to the gradient $\vec{g} = \vec{\nabla}\omega$ in the external magnetic field. This damping factor (measured in spin-echo experiments) is a sensitive probe of the impurity velocity $\vec{v}(t)$ and hence of the impurity mobility or diffusion.

III. CLASSICAL DIFFUSION

The classical method for impurities to diffuse through solids[7] is to "jump" over a barrier (energy Q) whenever enough thermal energy is present (probability proportional to e^{-Q/k_BT}). This leads to a diffusion coefficient of the form

$$D = a^2 \nu e^{-Q/k_BT} \ , \tag{12}$$

where a is the lattice parameter and ν is a vibrational-attempt frequency.

The damping factor $G(t)$ can be written in terms of the diffusion constant D by using the following argument. In the classical Brownian diffusion of impurities $\vec{v}(t)$ is a Gaussian stochastic process.[8] Therefore Eq. (11) may be written

$$G(t) = \{\exp -\tfrac{1}{2}\langle [\int_0^t dt_2 \int_0^{t_2} dt_1 \ \vec{g}\cdot\vec{v}(t_1)]^2\rangle\}. \tag{13}$$

Furthermore the velocity autocorrelation function

$$\phi(t - t') = \langle \vec{g}\cdot\vec{v}(t')\, \vec{g}\cdot\vec{v}(t')\rangle \tag{14}$$

determines the diffusion constant via the Einstein-Kubo relation,[9]

$$\int_0^\infty \phi(t)dt = g^2 D \ . \tag{15}$$

Equations (13)–(15) imply that

$$G(t) = e^{-g^2 D t^3/12} \quad \text{(classical diffusion)} \tag{16}$$

as $t \to \infty$. The exponential t^3 decay of Eq. (16) associated with spin-echo experiments is well known.[10] Our derivation is somewhat unusual since we have written the general equations in a form also applicable to the quantum-mobile situation.

IV. QUANTUM MOBILITY

We now wish to evaluate $G(t)$ for temperatures sufficiently low so that D [see Eq. (12)] can be neglected. The quantum method of diffusion is to "tunnel through" (as opposed to "jumping over") energy barriers. In a perfect crystal this leads to the energy bands discussed in Sec. I. The velocity of a single quantum-mobile impurity in a perfect crystal is not time dependent, i.e.,

$$\vec{v}_k = \hbar^{-1} \frac{\partial E(\vec{k})}{\partial(\vec{k})} \quad . \tag{17}$$

Equation (11) then reads

$$G(t) = \sum_{\vec{k}} f[E(k)] \exp(-\tfrac{1}{2} i\vec{g} \cdot \vec{v}_k t^2) \quad , \tag{18}$$

where $f(E)$ is the probability of finding the impurity with energy E. If $T \gg T_0$, then all states $\Psi_{\vec{k}}$ within the mobility band are equally probable. In that case

$$G(t) = \frac{v_{\text{cell}}}{(2\pi)^3} \int_{\text{BZ}} d^3k \exp\left(-i\vec{g} \cdot \frac{\partial E}{\partial \vec{k}} \frac{t^2}{2\hbar}\right) . \tag{19}$$

The integral in Eq. (19) can be explicitly evaluated for the case of cubic crystals with nearest-neighbor hopping (i.e., tunneling or exchange):

$$E(\vec{k}) = -(B - \Delta) - \tfrac{1}{3}\Delta(\cos k_x a + \cos k_y a + \cos k_z a) \ . \tag{20}$$

In Eq. (20), B is the binding energy of the impurity and Δ is the width of the energy band. Equations (19) and (20) imply[11] (with $\vec{g}$ parallel to the x axis)

$$G(t) = J_0(t^2 a g \Delta/6\hbar) \quad \text{(quantum mobility)} \ , \tag{21}$$

where

$$J_0(y) = \frac{1}{2\pi} \int_{-\pi}^{+\pi} e^{-iy \sin\theta} \, d\theta \tag{22}$$

is an oscillatory Bessel function.[12] The oscillations of the quantum mobile $G(t)$ [Eq. (21)] are qualitatively different than the classical diffusion $G(t)$ [Eq. (16)].

V. EXPERIMENTAL IMPLICATIONS

The relaxation time associated with classical-diffusion spin-echo damping is given by

$$t_{\text{diff}} = (g^2 D)^{-1/3} \quad \text{(classical diffusion)} \ . \tag{23}$$

The relaxation time associated with typical *oscillatory* quantum-mobile spin-echo damping is given by

$$t_{\text{mobile}} = (\hbar/ag\Delta)^{1/2} \quad \text{(quantum mobility)} \ , \tag{24}$$

where a is the lattice parameter and $\Delta = k_B T_0$ is the width of the mobility band. Equation (23) has been the basis of some of the most accurate determinations of diffusion constants ever performed in laboratories. Equation (24) has not yet been experimentally observed. However the oscillatory behavior of the damping should be evident whenever $t_{\text{mobile}} \ll t_{\text{diff}}$. In principle this implies that oscillatory damping factors can be observed if the quantum-mobile band thickness obeys

$$\Delta \gg \hbar(D^2 g)^{1/3}/a \ . \tag{25}$$

With typical values for (i) diffusion constants at liquid-helium temperatures [using Eq. (12) to extrapolate to low T], (ii) lattice parameters, and (iii) laboratory magnetic field gradients, Eq. (25) implies that mobility widths of $\Delta/k_B \gtrsim 10^{-5}$ °K can be detected by these methods.

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