$(^3\text{He})_2$ Molecules in Solid ^{4}He[†]

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The general features of $T_1(\omega)$ data on dilute ^{3}He in solid ^{4}He are explained in terms of coupled rotation-translation motions of $(^3\text{He})_2$ molecules bound together by the elastic ^{3}He-^{3}He interaction. As the concentration of ^{3}He is lowered the molecular motions become two-dimensional and give rise to the anomalous structure observed in the $T_1(\omega)$ spectrum.

Some time ago it was suggested that defects in the quantum crystals should be described by nonlocal single-particle excitations.[1,2] The essential physical idea behind this suggestion was that in the quantum crystals the large zero-point motion of the atoms would permit particle tunneling (for a vacancy) or interchange (for a ^{3}He impurity in ^{4}He) so that a localized picture of a vacancy or an impurity must give way to a Bloch-state picture; the vacancy and isotopic impurity become vacancy waves and mass fluctuation waves (MFW). It was recognized that the ideal system in which to seek evidence of MFW would be dilute ^{3}He in ^{4}He. The early experiments of Richardson and co-workers[3] on dilute ^{3}He in ^{4}He found ample evidence for ^{3}He-^{4}He tunneling. These experiments were followed by the complete series of measurements by Richards, Pope, and Widom[4] on the diffusion constant D, the longitudinal relaxation time $T_1(\omega)$, and the transverse relaxation time T_2. (See also the work of Grigor'ev, Essel'son, and Mikheev[5] on D that is complementary to that of Richards *et al.*) Although the data of Richards *et al.* were qualitatively in agreement with a MFW description of the ^{3}He-^{4}He motion, quantification of the theory led to an implausibly low rate of ^{3}He-^{4}He tunneling. Landesman and Winter[6] suggested that an interaction between ^{3}He atoms could be of importance in describing the dilute mixtures. A model of the dilute mixtures which treats the ^{3}He atoms as interacting strongly with one another because of the long-range elastic interaction has successfully given a qualitative and quantitative description of much of the data.[6-8] As a consequence of this success a strong-interaction model has begun to supersede the simple MFW model of dilute ^{3}He in solid ^{4}He.

The purpose of this paper is to describe a theory of $T_1(\omega)$ for dilute ^{3}He in ^{4}He with the strong-interaction model. We take the elastic ^{3}He-^{3}He interaction to bind pairs of ^{3}He atoms together as $(^3\text{He})_2$ molecules. By virtue of the tunneling motion of either of its constituents a $(^3\text{He})_2$ molecule undergoes discrete rotation-translation motions through the solid ^{4}He medium. We compare our theory of $T_1(\omega)$ with the recent experiments of Richards *et al.*[9] We are able to explain the anomalous "resonant" features in that data with an interesting piece of physics. As the ^{3}He concentration becomes less than 10^{-3} we find that the molecular motions through the ^{4}He medium become confined to two-dimensional planes.

A system of N_3 ^{3}He atoms in solid ^{4}He at concentration $x_3 = N_3/(N_3+N_4) \ll 1$ is described by[7]

$$H = \sum_{RR'} t(RR') b_R^\dagger b_{R'} + \sum_{RR'} V(RR') n(R) n(R'), \tag{1}$$

where $n(R) = b_R^\dagger b_R$, $b_R^\dagger$ creates a ^{3}He atom at lattice site R, $t(RR')$ is the tunneling rate of ^{3}He through ^{4}He, $|t(RR')| = J_{34}$, and $V(RR') = V_0 \Delta^3 / |R - R'|^3$ is the elastic interaction between ^{3}He atoms on R and R'. We expect $J_{34}/V_0 \lesssim 10^{-2}$. We want to calculate $T_1(\omega)^{-1}$, the rate of relaxation of the magnetization. Relaxation of the magnetization is due to the flipping of individual ^{3}He spins. The spin of a ^{3}He atom flips because of fluctuations of the dipolar field on the atom. The relevant quantity is the square of the dipolar field which falls off as r^{-6} so that the important contributions are from the near neighbors to any atom. But the near neighbors of an atom are bound to it by the elastic interaction. Thus the important fluctuations of the dipolar field on an atom are those associated with its tumbling with a near neighbor to which it is elastically bound as a $(^3\text{He})_2$ molecule. The appropriate expression for the relaxation time[10] is

$$\frac{1}{T_1(\omega)} = \sum_{q=1}^{2} q^2 \frac{1}{N_3} \sum_{i<j} \int_{-\infty}^{\infty} e^{iq\omega t} \langle\langle F_{-q}^{ij}(0) F_q^{ij}(t) \rangle\rangle . \tag{2}$$

Here F_q^{ij} is the spatial component of the dipolar interaction corresponding to the flipping of q spins.[10]

The motion of a molecule is most appropriately followed on the center-of-mass (c.m.) lattice. The c.m. lattice sites are given by $\vec{\tau}_p = (\vec{R}_i + \vec{R}_j)/2$, where $\vec{R}_i$ and $\vec{R}_j$ are two near-neighbor lattice sites of the hcp lattice. The sites of the c.m. lattice correspond to a particular molecular location in the real crystal and a corresponding orientation. The elements of this description of motion in the hexagonal plane of an hcp crystal are shown in Fig. 1.

Molecular motion through the c.m. lattice is described by

$$H_{\text{c.m.}} = \sum_{\vec{\tau}_p, \vec{\tau}_{p'}} t(\vec{\tau}_p, \vec{\tau}_{p'}) C_{\tau_p}{}^{\dagger} C_{\tau_{p'}} + V, \tag{3}$$

where $|t(\vec{\tau}_p, \vec{\tau}_{p'})| = J_{34}$ for exchange-connected neighbors and $C_\tau{}^\dagger$ creates a molecule at site $\vec{\tau}$. We have removed part of the elastic interaction of Eq. (1) by forming the molecule; the remainder of this interaction, V of Eq. (3), is the elastic field of other ^{3}He atoms through which the molecule moves. At concentrations $x_3 \gtrsim 10^{-3}$ the molecule sees a sufficiently large elastic field from the other ^{3}He atoms that it is able to undergo only hindered rotation through the crystal. Following the treatment of this phenomena by Abragam[10] we have

$$[T_1(\omega)]^{-1} \propto (\omega^2 \tau_{34})^{-1}, \tag{4}$$

where $\tau_{34}{}^{-1}$ is the hopping rate associated with diffusion of the molecules. We might expect the molecular diffusion rate to be similar to the single-particle diffusion rate seen directly in diffusion data.[4,5] The consistency of $T_1(\omega)$ and $T_2(0)$ data[5] and of $T_2(0)$ and D data[4] suggest that this is approximately correct.[11] As the ^{3}He concentration is reduced much below 10^{-3} we expect the hindered rotation of the $(^3\text{He})_2$ molecule to give way to the coupled translation-rotation motion of a free molecule. To explore this limit we ignore the interaction in Eq. (3) and find the set of single-particle excitations that describe $(^3\text{He})_2$ molecular motion on the c.m. lattice. These excitations are created by

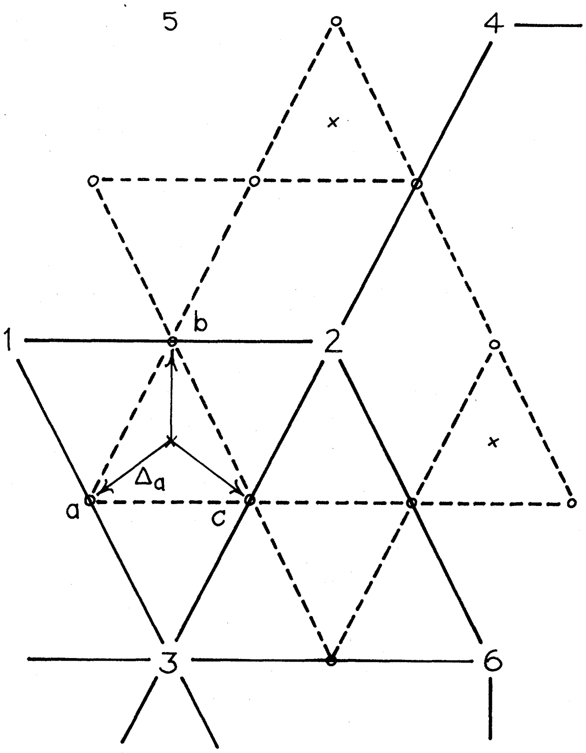

FIG. 1. Center-of-mass lattice for two-dimensional motion. A molecule is formed by a pair of ^{3}He atoms on two near-neighbor sites, e.g., 1 and 3. The molecule moves by tunneling of either atom to a mutual near neighbor (1, 3) → (1, 2). The center of mass of the molecule moves from a to b. When the molecule is on (1, 2) it cannot dissociate by going to (1, 4) because the elastic interaction makes (1, 4) an energetically disallowed configuration. The center-of-mass lattice is connected as shown by the dashed lines.

$$C_{k\nu}{}^{\dagger} = \sum_{i,a} \exp(i\vec{k}\cdot\vec{\tau}_i) U_{a,\nu} C_{\tau_p}{}^{\dagger}, \tag{5}$$

where $\vec{\tau}_p = \vec{\tau}_i + \vec{\Delta}$, $\vec{\tau}_i$ locates a unit cell in the c.m. lattice, $\vec{\Delta}_a$ locates a particle in the unit cell, $\vec{k}$ is the wave vector for the unit-cell lattice, ν is a band index, and $U_{a\nu}$ diagonalizes the cell Hamiltonian (see Fig. 1). In terms of the plane-wave excitations for the molecule, Eq. (2) for $T_1(\omega)$ becomes

$$[T_1(\omega)]^{-1} = \bar{M}_2 \pi x_3 \sum_{q=1}^{2} q^2 \sum_{\vec{k}} \sum_{\nu\nu'} |F_q(k)_{\nu\nu'}|^2 \delta(\omega_{k\nu} - \omega_{k\nu'} + q\omega) \Big[\sum_q q \sum_k \sum_{\nu\nu'} |F_q(k)_{\nu\nu'}|^2\Big]^{-1}, \tag{6}$$

where the matrix elements of the interaction are between states at the same wave vector but in different energy bands. This is because the matrix elements of F_q have the periodicity of the c.m. lattice. $\bar{M}_2$ is the second moment appropriate to near neighbors only. The proportionality of $T_1(\omega)$ to x_3 in Eq. (6) should be noted. If the $(^3\text{He})_2$ molecules were permanently bound, T_1 would be independent of x_3.

We assume that the molecular bonds are regularly formed and broken so that ^{3}He attoms sample all configurations with equal probability. However, relaxation occurs almost exclusively in the molecular state, hence the x_3 dependence. The breaking of a bond could be caused by interaction with other ^{3}He atoms or phons. However the precise process is unknown.

We have calculated the excitation spectrum for molecular motion through the c.m. lattice. Using these excitations we have calculated $T_1(\omega)^{-1}$ from Eq. (6). We describe the results of this calculation by writing Eq. (6) in the form

$$\frac{1}{T_1(\omega)} = \pi \bar{M}_2 x_3 \frac{\hbar}{J_{34}} L_3(\omega) \tag{7}$$

and showing $L_3(\omega)$ in Fig. 2. The function $L_3(\omega)$ is well approximated by $L_3(\omega) \propto \exp(-\omega/\bar{\omega})$ with $\bar{\omega} = 2.0 J_{34}$. But with $L_3(\omega) \propto \exp(-\omega/\bar{\omega})$ Eq. (7) is very similar to the empirical equation used by Richards *et al.* to fit the background $T_1(\omega)$ data.[9] The choice $J_{34} = 0.6$ MHz gives excellent quantitative agreement. This result confirms the essential features of the approximate treatment of the $(^3\mathrm{He})_2$ molecular explanation of $T_1(\omega)$ formed by one of us (W.J.M.)[9] But the most striking feature of the $T_1(\omega)$ data is the resonantlike anomalies near $\omega/2\pi = 1.5$ MHz and $\omega/2\pi = 3.0$ MHz that become more prominent as $x_3 \to 0$. We believe we understand the source of this behavior.

On the c.m. lattice there are two inequivalent orientations for a $(^3\mathrm{He})_2$ molecule. This inequivalence comes from the difference in location of the second and further neighbors of a molecule for the two orientations of molecules. The hcp crystal is made up of hexagonal planes stacked as *ABAB*... An *A*-*A* molecule (both atoms in an *A* plane) has elastic energy V_{AA} different from that of an *A*-*B* molecule, V_{AB}. As the elastic energy is of order V_0 we expect that an *A*-*A* molecule will have energy different from an *A*-*B* molecule by an amount much greater than $|J_{34}|$, i.e., $|J_{34}| \ll |V_{AA} - V_{AB}|$. Thus direct tunneling from *A*-*A* to *A*-*B* sites is forbidden. Such tunneling can occur with phonon assistance—we estimate this process to be very slow—or through the compensation of $V_{AA} - V_{AB}$ by the elastic field of distant neighbors. But as the concentration is lowered this latter mechanism fails and the molecules on *A*-*A* sites must remain on *A*-*A* sites and the molecules on *A*-*B* sites must remain on *A*-*B* sites. But the *A*-*A* sites are connected among themselves by tunneling at rate J_{34} in a plane perpendicular to the *c* axis of the c.m. lattice; so also are the *A*-*B* sites. Thus as $x_3 \to 0$ we expect the molecules to be forced into two-dimensional motion parallel to the hexagonal planes.

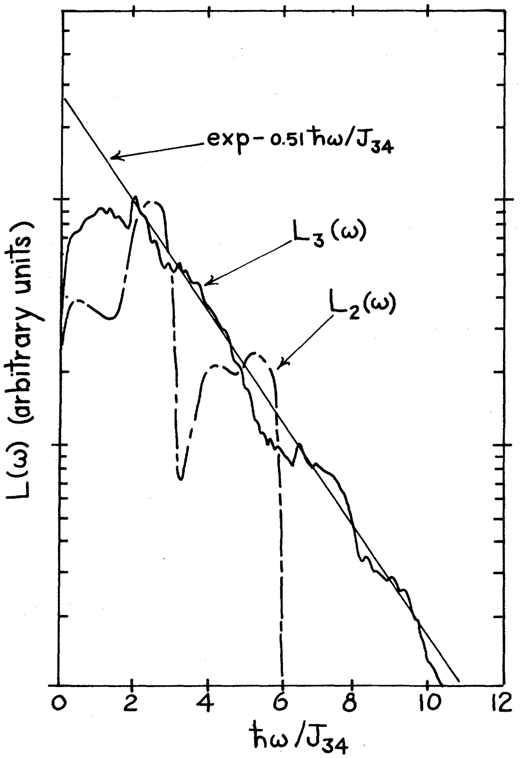

FIG. 2. Spectral density histograms. The function $L_3(\omega)$ is plotted as a function of $\hbar\omega/J_{34}$. The straight line drawn through $L_3(\omega)$ is given by $L_3(\omega) \propto \exp(-0.50 \times \hbar\omega/J_{34})$. Comparison with the empirical formula of Richards *et al.*, $L(\omega) \propto \exp(-\omega/\omega_{34})$, $\omega_{34} = 1.17$ MHz, leads to $J_{34} = 0.6$ MHz $= 2.7 \times 10^{-5}$ K. The function $L_2(\omega)$ is plotted as a function of $\hbar\omega/J_{34}$. [Although it is as structured as $L_3(\omega)$ we have smoothed $L_2(\omega)$ for clarity of presentation.] With the choice $J_{34} = 2.7 \times 10^{-5}$ K the 2ω and ω structure (Ref. 12) in $L_2(\omega)$ occurs at 1.1 MHz $\lesssim \omega \lesssim 1.8$ MHz and 2.2 MHz $\lesssim \omega \lesssim 3.6$ MHz. These are frequency intervals in which structure is seen in the data of Richards *et al.* All calculations involve a powder average.

We have calculated the excitation spectrum for molecular motion on this planar c.m. lattice. One plane of this lattice is shown in Fig. 1. Using these excitations we have calculated $T_1(\omega)^{-1}$ from Eq. (6). The results are written in the form of Eq. (7) with $L_2(\omega)$ replacing $L_3(\omega)$; $L_2(\omega)$ is shown in Fig. 2. To set the frequency scale of $L_2(\omega)$ we choose $J_{34} = 0.6$ MHz in accord with the choice made above to fit $L_3(\omega)$ to the background. We see that in $L_2(\omega)$ there is structure at 1.1 MHz

$\leq \omega \leq 1.8$ MHz and 2.2 MHz $\leq \omega \leq 3.0$ MHz precisely where structure[12] is observed in the data of Richards *et al.* We take this agreement to confirm our belief that the $(^3\mathrm{He})_2$ molecules move two dimensionally as $x_3 \rightarrow 0$ and to confirm the choice $|J_{34}| = 0.6$ MHz.

An interesting feature of the experimental data[9] is that 50% of the spectral density is at low frequency, $\omega \lesssim 10^{+4}$ Hz, and 50% is in the large-ω structure discussed in this paper. $L_2(\omega)$ as shown in Fig. 2 accounts for just 50% of the total spectral density at $\omega \neq 0$. Thus the planar calculation of $T_1(\omega)$ is in good quantitative agreement with experiment. The planar calculation has an additional 33% of the spectral density in a δ function at $\omega = 0$. The remaining 17% of the total would be found by considering neighbors other than nearest and is expected to contribute to the $\omega \approx 0$ region. The δ function is expected to be broadened to about 10^4 MHz by complex and slow motions we have not considered here.

A complete description of the $T_1(\omega)$ data requires a combination of two dimensional motion, hindered rotations, and three-dimensional motion with the latter two providing a bit more background density than the two-dimensional motion in $L_2(\omega)$ seems to account for by itself at the concentrations studied by Richards *et al.*

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[11] The exact frequency dependence of $T_1(\omega)$ at large ω seen in experiment (Ref. 3) agrees quite well with the theory of Abragam at concentrations above 10^{-3}; at lower concentrations the frequency dependence becomes somewhat stronger.

[12] The two-dimensional motions lead to a single peak of transitions. In $T_1(\omega)^{-1}$ there will then be two peaks, one corresponding to $q = 1$ in Eq. (2) and the other to $q = 2$. See Ref. 10.

Nonlinear Parallel Ringing of Magnetization in Superfluid ^{3}He†

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Experiments based on an analogy to the ac Josephson effect have shown in both ^{3}He-A and ^{3}He-B that a pairing theory of the superfluidity of ^{3}He is essentially correct. Additional observations of parallel ringing are not in agreement with the simple "pendulum models" used to describe nonlinear dynamic magnetic effects.

According to current theoretical concepts[1] as supported by experiment,[2] superfluid ^{3}He consists of one or more interpenetrating and weakly coupled supefluids as well as a normal fluid. A BCS-like pairing theory is used to describe the superfluidity with ^{3}He-A having both $\uparrow\uparrow$ and $\downarrow\downarrow$ triplet-paired superfluids and ^{3}He-B both of these plus an $\uparrow\downarrow$ paired superfluid as well. The weak coupling between superfluids is provided by a coherent dipolar interaction. In the present work we have attempted to test the pairing theory by performing an experiment analogous to the one described by Josephson[3] for two weakly coupled superconductors with a potential difference V between them and a resulting ac supercurrent of frequency $2eV/h$. In the case of ^{3}He the sudden