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Vacancy-induced nuclear-spin–lattice relaxation in solid ^{3}He

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New experimental data are presented for the temperature-dependent vacancy-induced nuclear-spin–lattice relaxation times in both the hcp and bcc phases of ^{3}He. Single-crystal specimens were studied over a range of temperature and magnetic field for which values of the activation energies Φ and the tunneling frequencies ω_V of vacancies could be obtained with an accuracy hitherto unattained. The values of Φ and ω_V deduced from the data are compared with previous values obtained from NMR measurements and x-ray diffraction.

I. INTRODUCTION

In quantum crystals such as the solid heliums, the zero-point kinetic motion of an atom amounts to almost 30% of the interatomic spacing and, as a consequence, there is a large probability that an atom in the neighborhood of a vacant lattice site (a vacancy) will tunnel from its own lattice site to the vacant site. The vacancies are mobile entities and recent theoretical arguments[1-3] suggest that their propagation through the crystal might be described in terms of vacancy waves. A direct result of the mobility of the vacancies is the modulation of the internuclear magnetic dipole-dipole interaction, and this provides a possible mechanism for nuclear spin relaxation, both transverse and longitudinal, in solid ^{3}He.

The aim of this paper is to present new data for both bcc and hcp phases of ^{3}He in the range of temperature and applied magnetic field where the dominant mechanism for spin relaxation is given by vacancy modulation of the nuclear dipolar fields. Relevant data have been available for several years,[4-9] but in view of the improved understanding of the physics of vacancies it was felt that there was a need to repeat the measurements for those conditions where the parameters characterizing the vacancies, the formation energy and the tunneling frequency, could be determined with greater accuracy.

The organization of this paper is as follows. Following a brief review of current knowledge concerning vacancies in solid helium and how information regarding their properties can be extracted from NMR experiments, we discuss the details of the experiments to be analyzed here, pointing out in which aspects they complement previously reported experiments. Finally, we present the values obtained for the formation energies and the tunneling frequencies of vacancies for different molar volumes and compare these with the results of previous experiments and with the theoretical predictions.

II. REVIEW OF PROPERTIES OF VACANCIES

A. Observation by x-ray diffraction

The most direct evidence corroborating the existence of thermal defects associated with the creation of vacancies in solid helium is probably that provided by x-ray diffraction.[9] By measuring the temperature dependence of the Bragg diffraction from a solid held at constant volume, Balzer and Simmons obtained a direct record of the variation of the lattice parameter a,

$$\delta a/a \simeq -\tfrac{1}{3}\delta x \ ,$$

where x is the net concentration of Schottky-type defects.[10] For a static vacancy with an energy of formation $k_B\Phi$ and an entropy of formation S_f this concentration is

$$x = e^{S_f/k_B}\, e^{-\Phi/T} \ .$$

We believe that the entropy S_f is negligible for the following reasons. First, in solid helium k_BT is always small with respect to most phonon frequencies in the crystal, either perfect or defective, and the vibrational entropy of formation is therefore vanishingly small. Second, the only remaining possibility for a finite S_f is associated with a lattice relaxation with a symmetry less than that of the perfect lattice. In the bcc lattice, calculations using the method of Hetherington[1] and improved calculations by Williams[11] lead to the conclusion that a vacancy with an axial lattice relaxation requires more energy than a vacancy with a cubic lattice relaxation. Consequently we omit the entropy of formation S_f. The results of Balzer and Simmons analyzed with a concentration

$$x = e^{-\Phi/T} \tag{1}$$

lead to the energies of formation given in Table I.

B. Specific heat

Earlier evidence supporting the existence of vacancies in solid helium originated from studies of the specific heat at constant volume of powdered

TABLE I. Values of the parameters characterizing vacancies in solid ^{3}He. Φ is the energy of formation of a vacancy, W is the activation energy observed experimentally, τ_0 is defined by Eq. (8), and ω_V is the tunneling frequency.

V (cm^3/mole)	Φ (K)	W (K)	τ_0 (psec)	$10^{-10}\omega_V$ (sec^{-1})	Reference
20.0	13				X-ray diffraction (Ref. 9), bcc with $S_f = 0$
20.5	11				
20.9	10				
20.18		13.20			Specific heat (Ref. 6), bcc as discussed in Ref. 12
21.46		10.49			
22.86		7.95			
23.80		6.64			
20	13.7	13.7		0.4	T_1 (ZE-VP) (Ref. 8), bcc as analyzed in text
20.12		13.6	10.6	1.8	T_1 (Z-VP) at 30.4 MHz, bcc (Ref. 4) as analyzed in Ref. 7
20.03		14.5	36	0.53	T_1 (Z-VP) at 80 MHz, bcc Fig. 1
21.10		9.6	34	0.55	
22.03		8.1	40	0.48	
23.05		7.3	30	0.63	
19.24		17.9	5		T_1 (Z-VP), 2–5 MHz, bcc Fig. 4
19.46		17.4	4		
18.82		34	3.2		T_1 (Z-VP) at 5.224 MHz, hcp (Ref. 5)
17.63		42.6	4.2		T_1 (Z-VP), 2–5 MHz, hcp Figs. 3 and 4
17.81		41.7	3.4		
18.07		39.2	3.2		
18.34		36.0	4.2		
18.49		35.2	3.4		
18.65		34.2	3.4		
18.95		33.7	2.6		
19.24		31.4	2.2		
19.46		30.1	2.8		

samples.[6] These measurements have been analyzed in terms of an excess specific heat arising from the thermal activation of vacancies

$$C_{\text{observ}} - C_{\text{phonons}} \simeq R(\Phi/T)^2 e^{-\Phi/T} \ .$$

Since C_{phonons} is not known independently, two unreliable assumptions have to be made[12] in order to analyze the data: first, the assumption of a Debye phonon spectrum for the lattice; second, the uncertainties in the Debye temperatures. The data are then interpreted in terms of an activation energy W:

$$C_{\text{observ}} - C_{\text{Debye}} \simeq R(W/T)^2 e^{-W/T} \ .$$

The values of W are given in Table I for the sake of completeness and the reader is referred to the review article of Trickey, Kirk, and Adams for details.[13]

C. NMR experiments

Studies of nuclear spin dynamics in NMR experiments are sensitive to the presence of vacancies only as a result of their mobility and the consequent time dependence of the position coordinates specifying the spin ensemble. Let us assume that a vacancy can migrate from a lattice site to a neighboring site with some characteristic frequency $1/\tau$. The ^{3}He atoms, as seen by NMR, will therefore have a temperature-dependent jump frequency $1/\tau_r$ proportional to the concentration x of vacancies:

$$1/\tau_r = x/\tau \ . \qquad (2)$$

Before raising the question of the physical origin of the characteristic vacancy frequency τ^{-1}, we recall how we observe the atomic jump frequency τ_r^{-1}. The difficulty in analyzing NMR experiments is that they measure τ_r rather than τ. Referring only to spin-lattice relaxation for the moment, there are two regimes where experiments yield information on τ_r: Depending on the temperature of the lattice, the Zeeman energy (Z) reaches thermal equilibrium as a result of its coupling with, and the interactions between, the vacancies (V), the exchange interactions (E) and the phonons (P).[14]

(1). The Z-VP regime. In the Z-VP regime[14] ($T > 1$ K), the weak link is the Zeeman vacancy coupling; the Pauli exchange interactions play no role, the vacancy-phonon coupling is strong, and the spin-lattice relaxation results from the modulation of the dipole-dipole interactions by the motion of the vacancies. The observed rate for this "liquidlike" relaxation can be written as a sum of spectral densities for the modulation:

$$1/T_1 = J_1(\omega) + 4J_2(2\omega) \ , \tag{3}$$

ω being the Larmor frequency.

The spectral densities are difficult to predict, but at high magnetic field ($\omega\tau_r \gg 1$), the atomic jump is a weak collision for the Zeeman system and T_1 is proportional to $\omega^2\tau_r$. For $\omega\tau_r \simeq 1$, the relaxation time goes through a minimum as a function of τ_r.

The frequency of modulation of dipole-dipole interaction is

$$\tau_{\mathrm{V}}^{-1} \simeq 2\tau_r^{-1} \ .$$

Assuming the spectral densities to be Lorentzian, as in Eq. (7.1) of Ref. 14,

$$J_m(\omega) = \frac{J_m^{\mathrm{V}}(0)}{1+\omega^2\tau_{\mathrm{V}}^2} \ , \quad m = 1, \ 2 \tag{4}$$

as in the model of Bloembergen, Purcell, and Pound,[15] henceforth referred to as the BPP model. For polycrystalline samples we have $J_1^{\mathrm{V}}(0) = J_2^{\mathrm{V}}(0) = \frac{2}{3}M_2\tau_{\mathrm{V}}$, where M_2 is the rigid-lattice second moment of the resonance line. At high magnetic fields the relaxation rate becomes

$$1/T_1 = \lambda(M_2/\omega^2\tau_r) \quad (\omega\tau_r \gg 1) \ , \tag{5}$$

where $\lambda = \frac{8}{3}$.

In an attempt to improve on the simple theory of BPP, Torrey[16] calculated the spectral densities by taking into account in a semiclassical way the microscopic details of the random walk of an atom jumping with an average frequency $1/\tau_r$. For a polycrystalline sample, Eq. (5) still holds for $\omega\tau_r \gg 1$ with a slightly different numerical coefficient, namely, $\lambda = 2.3$.

(2). The ZE-VP regime. In the ZE-VP regime,[14] at low temperatures, the bottleneck for the flow of energy occurs between the exchange system and the vacancies which are in strong thermal contact with the phonons. For very pure samples of ^{3}He (^{4}He concentrations $\langle$1 ppm), the atomic jump is a strong collision for the exchange system,[17] and one observes a relaxation rate

$$\frac{1}{T_1} = \left(\frac{3J^2}{3J^2 + \omega^2/4}\right)\frac{1}{T_{\mathrm{EL}}} \ . \tag{6}$$

Equation (6) is written for the bcc lattice; J is the exchange interaction. The quantity in parentheses is a "topological" factor determined by the heat capacities of the Zeeman bath and of the exchange bath. T_{EL} is the intrinsic exchange-lattice relaxation due to vacancy-induced atomic jumps, and for the bcc lattice[14]

$$T_{\mathrm{el}} = \tfrac{4}{7}\tau_r \ . \tag{7}$$

D. Tunneling frequency

Having recalled what information is provided by NMR experiments on τ_r, we now discuss the physical origin of this jump time. Experimentally it obeys the Arrhenius relation

$$\tau_r = \tau_0 e^{W/T} \ . \tag{8}$$

Let us consider the mechanism for transferring a vacancy to a neighboring site. Either one has a classical diffusion, or the vacancy tunnels to the neighboring site. In the former case, the vacancy requires sufficient thermal energy to pass over a potential barrier of height $k_B\Phi_m$; then $1/\tau \propto e^{-\Phi_m/T}$ and $W = \Phi + \Phi_m > \Phi$, where we recall that Φ is the energy of formation. In the latter case, the vacancy tunnels through that barrier, as suggested in the Introduction. The characteristic frequency $1/\tau$ does not depend on temperature if one neglects the scattering of phonons by the vacancy.[18] Consequently, the activation energy k_BW measured by NMR arises only from the vacancy concentration and is equal to the energy of formation $k_B\Phi$, measured by x-ray diffraction. In the remainder of this section we assume a quantum tunneling of vacancies. Let ω_{V} be the tunneling frequency of a vacancy between two neighboring sites.[1,14] The preexponential factor τ of the temperature-dependent jump time is then simply the inverse characteristic vacancy frequency,

$$1/\tau = A\omega_{\mathrm{V}} \ , \tag{9}$$

where A is a constant, calculated in Ref. 18 for the bcc lattice by the approximate method of moments and found equal to 5.2.

E. Vacancy waves

At this point we should consider the possibility of the existence of vacancy waves in solid ^{3}He,[1-4] which should be good quantum modes at sufficiently low temperatures, although there is at present no direct experimental evidence supporting this conjecture. The idea is that vacancies form a band of delocalized states whose energy for small wave vector $\vec{q}$ obeys the dispersion relation

$$\hbar\omega_q = k_B\Phi - \tfrac{1}{2}k_B\Delta(1 - \tfrac{1}{6}a^2q^2 + \cdots) \ ,$$

where a is the nearest-neighbor distance. The bandwidth $k_B\Delta$ is proportional to ω_{V}. The derivation of Δ in unpolarized ^{3}He is rather subtle[2];

Brinkman and Rice[19] have shown in their equation (2.25) that

$$k_B\Delta = 4(z-1)^{1/2}\hbar\omega_V \ , \tag{10}$$

where z is the number of nearest neighbors.

The assumption of vacancy waves has some bearing on the discussion of the results. We postulate here that Eqs. (2) and (3) still hold, except that x and τ have to be defined! So long as $T \gg \Delta$, the previous formulas remain true: We can use Eqs. (1) and (9) for the vacancy concentration and the vacancy characteristic frequency. If the temperature is comparable to or smaller than the bandwidth one has to remember that the vacancy concentration is really

$$x = N^{-1}\sum_q e^{-\hbar\omega_q/k_BT} \ , \tag{11}$$

which can be written as[9]

$$x = F(T)e^{-\Phi/T} \ . \tag{12}$$

The factor $F(T)$, which tends to unity as $T\rightarrow\infty$, depends on the extent to which the band is filled. If $T \ll \Delta$,

$$F(T) = (V/Na^3)(3T/\pi\Delta)^{3/2}e^{\Delta/2T} \ . \tag{13}$$

Presumably $1/\tau$ is always of the order of ω_V, so that the ^{3}He jump time varies, when $T \ll \Delta$, as

$$\tau_r \propto T^{-3/2}e^{(\Phi-\Delta/2)/T} \ . \tag{14}$$

In practice it is very difficult, using the experimental data, to differentiate between the Arrhenius law, whose temperature dependence is given by a simple exponential factor, and the temperature dependence such as that given by Eq. (14).

III. EXPERIMENTAL METHODS

All the samples for which new data are reported in this paper consisted of crystals grown at constant pressure using a controlled temperature gradient. Such a technique, well known by experimentalists studying thermal conductivity and ion mobility in solid helium,[20,21] should yield single crystals, although it was not possible to verify this by means of x-ray diffraction in our NMR experimental arrangements.

Two distinct systems were used to perform experiments.

(a) The first was a low-field spectrometer[22] using a conventional electromagnet for which data were taken with a pulse spectrometer operating at 2.125, 3, or 5 MHz, over a temperature range extending from 4.2 to 1.2 K and at pressures which can be as high as 200 bars ($V \simeq 17.6$ cm^3/mole).

(b) The second apparatus[23] operated at high fields, using a superconductive magnet and a cw spectrometer working at 80 MHz. A temperature range of 0.35–2.5 K was investigated using a liquid-^{3}He evaporation refrigerator.

In both systems the crystals were grown in Kel-F cells containing a metallic cold point linked to either a bath of liquid ^{4}He or liquid ^{3}He (according to the temperature range under investigation), the temperature gradient being regulated by a feedback system. The temperatures were recorded by means of carbon resistors calibrated against the ^{4}He and ^{3}He vapor-pressure temperature scales. We were able to monitor the crystal growth at constant pressure by selective saturation of the liquid NMR absorption signals. Measurements of the pressure (as applied externally) and the temperature were compared with published P-T phase diagrams[24] and found to be consistent to within 50 mK, enabling the molar volumes to be determined from Grilly's V-T phase diagrams[24] with an accuracy of approximately 0.1%. ^{4}He concentrations were always less than 250 ppm.

The new aspects of the experiments reported here are the following. (i) Systematic measurements in a high magnetic field (25 kG). Few data have been reported for the relaxation times at such high fields. These include one publication devoted to Zeeman-exchange (Z-EP) relaxation[23] and the high-magnetic-field pressure measurements of Kirk and Adams.[25] The aim of these measurements was to ascertain whether the models outlined in Sec. II could still be used to describe the relaxation in this field domain and, if so, to deduce Φ and τ_0 with a greater accuracy than previously realized. The observed values of T_1 in the Z-VP regime extend over approximately three decades at $V = 20$ cm^3/mole. (ii) The constant-pressure crystal-growing technique. (iii) The data obtained in the hcp phase, for which few observations have been published. (iv) The observed anisotropy of the relaxation times using the low-field apparatus, where the magnetic field can be rotated with respect to the sample in a plane perpendicular to the axis of growth.[22]

IV. RESULTS

We now present the results of the T_1 measurements obtained using both systems and analyze them to obtain information for the jump time defined by Eq. (8) and making use of the BPP equation (5). For the bcc lattice we will find that the activation energy defined in Eq. (8) is close to the formation energy Φ for a vacancy. We therefore consider that any difference between Φ and W is of experimental origin only. We identify the preexponential factor τ_0 (measured experimentally) with the inverse τ of the characteristic vacancy frequency defined in the introduction and make use of the relation (9) to deduce ω_V. This relation (9) is the result of a calculation based on the method of moments and, as such, should be taken with caution. The data were analyzed using the BPP model rather than the theory of Torrey, both for the sake of simplicity and because Torrey's theory is not necessarily applicable in the case of vacancy waves. As a result of the corresponding value of λ entering in Eq. (5) this reflects on the values deduced for ω_V. The latter cannot, however, be determined with the same accuracy as those for the activation energies (W or Φ). As far as the activation energy is concerned, Torrey and BPP's formulas give, of course, the same value.

At present, only NMR experiments have provided information on vacancies in the hcp phase; thermodynamic measurements are frustrated since the Debye temperatures are comparable to the formation energies. Although the sensitivity of NMR to the presence of vacancies is obviously high, NMR alone is not really sufficient to determine the mechanism for the motion of vacancies, since we have no independent experimental information for the energy of formation of vacancies Φ. Consequently, we analyze the relaxation times with a correlation time such as (8) and call τ_0 and W the preexponential factor and the activation energy, respectively.

One possible criticism of the use of Eqs. (4) and (5) is that they are apparently written for a polycrystalline sample, which is contradictory to the constant-pressure crystal-growing technique previously described, which should produce single crystals. The answer to that criticism is both theoretical and experimental. The anisotropy of relaxation times has been calculated by Harris[26] for exchange modulation of the dipolar interactions and the calculation can be generalized to a spectral density such as (4). The results are the following.[22] First, T_1 is always more isotropic in the hcp lattice than in the bcc lattice. Second, for a vacancy modulation of the dipolar interaction (Z-VP), the anisotropy is less than that for an exchange modulation of the same interaction (Z-EP). If $\omega\tau_r \gg 1$, the maximum expected anisotropy is 0.15 for the bcc lattice and 0.06 for the hcp lattice.

Experimentally, we did investigate the anisotropies of T_1 using the low-field apparatus, rotating the magnetic field in a plane perpendicular to the crystal-growing axis,[22] and could, in fact, detect an anisotropy as large as 0.3 for the Zeeman-exchange cross relaxation time (Z-EP regime of Guyer, Richardson, and Zane[14]). For the vacancy-induced Zeeman relaxation time (Z-VP regime of Ref. 14), the observed T_1 anisotropies were even smaller. We then found that it was legitimate to analyze all data with the equations presented in Sec. II for a polycrystalline sample.

A. High-field data

Figure 1 shows the spin-lattice relaxation times measured at 80 MHz for molar volumes of 20.03, 21.10, 22.03, and 23.05 cm^3. It shows the temperature-dependent T_1 and, for the three largest molar volumes, the temperature-independent Zeeman-exchange plateau (Z-EP) previously published.[23] The solid curves are derived using the BPP model, as discussed above, to provide the best fit in the temperature-dependent region.

The activation energies W obtained from the data using this procedure are given in Table I and are compared in both Table I and Figure 2 with the activation energies previously reported. The values are close to those of Balzer and Simmons,[9] except for $V = 20.03$ cm^3/mole, where the difference is not necessarily larger than realistic error flags. This leads us to believe that we do have a tunneling motion for the vacancies and we use the preexponential factor $\tau_0 \equiv \tau$ to determine ω_V (see Table I). This tunneling frequency is of the order of 0.5×10^{10} sec^{-1}: Within the limited accuracy of our experiments, as far as the preexponential factor is concerned ($\simeq 30\%$), we cannot draw any conclusion on the volume dependence of ω_V, which is roughly constant for $20 < V < 23$ cm^3/mole. This value of ω_V is somewhat smaller than the value deduced from the experiments of Goodkind and Fairbank[4] by Hartmann's analysis.[7] We compare our value of ω_V with the following analysis of Giffard's result[8] for the vacancy contribution to the intrinsic exchange-lattice relaxation time (ZE-VP regime) in the bcc lattice:

$$T_{EL}^{-1} = 3.3\times10^{10}\, e^{-13.7/T}\ \text{sec}^{-1}.$$

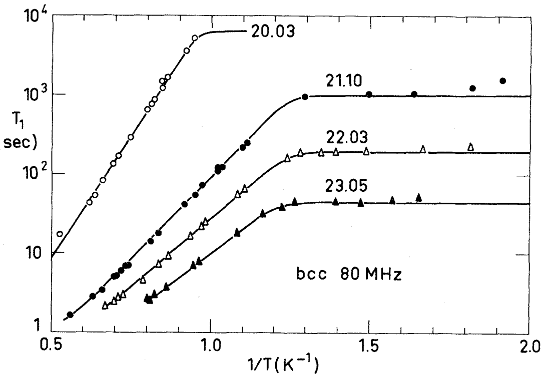

FIG. 1. Temperature dependence of the nuclear-spin-lattice relaxation times in bcc ^{3}He (high-field data). Legends refer to differing molar volumes designated in the figure.

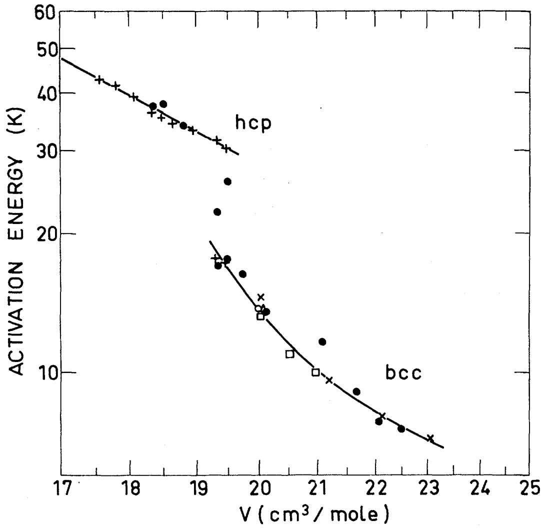

FIG. 2. Vacancy activation energy as a function of molar volume V. +, NMR T_1 (Z-VP) at 2–5 MHz; ×, NMR T_1 (Z-VP) at 80 MHz; △, NMR T_1 (Z-VP) at 30.4 MHz (Ref. 7)]; ●, NMR and diffusion data (Ref. 5); ○, NMR T_1 (ZE-VP) (Ref. 8) as analyzed in text; x-ray diffraction (Ref. 9).

This value was obtained for $0.43 < T < 0.55$ K; let us estimate the vacancy concentration using the band-model calculation above [see Eqs. (12) and (13)]. The result is

$$x = 4(T/\pi\Delta)^{3/2} e^{-(\Phi-\Delta/2)/T} , \tag{15}$$

where the vacancy bandwidth $k_B\Delta$ is given by Eq. (10). Combining Eqs. (2), (7), (9), and (15), we can write

$$T^{-1}_{\mathrm{EL}} = A\omega_V^{-1/2} \frac{7^{1/4}}{8} \left(\frac{k_B T}{\pi\hbar}\right)^{3/2} \exp\left(-\frac{(\Phi-\Delta/2)}{T}\right) .$$

Identifying this expression with Giffard's result for $T = 0.5$ K and taking $A = 5.2$ (with a certain arbitrariness), we obtain $\omega_V = 0.9\times10^{10}$ sec^{-1} and $\Phi = 14.1$ K. If we interpret Giffard's result with Eq. (1) instead of Eq. (15), we obtain $\omega_V = 0.4 \times10^{10}$ sec^{-1} and $\Phi = 13.7$ K, which are indeed close to our values (see Table I and Fig. 2).

B. Low-field data

Figures 3 and 4 show some typical spin-lattice relaxation times measured at 2.125, 3, and 5 MHz. In Fig. 4, for molar volumes 19.24 and 19.46 cm³, discontinuities in T_1 are observed when crossing the hcp-bcc transition lines at constant volume. These discontinuities fall within the temperature range for the transition reported by Straty and Adams.[27]

Using the BPP equation (5), the data of Figs. 3 and 4 were analyzed in terms of an activation energy W and a preexponential factor τ_0 for the correlation time, both of which are given in Table I. The solid curves in the figures represent the best fit to the data. Fewer data points were obtained in the bcc phase and, as a result, the values obtained for W and τ_0 are not as reliable as those quoted for the hcp phase.

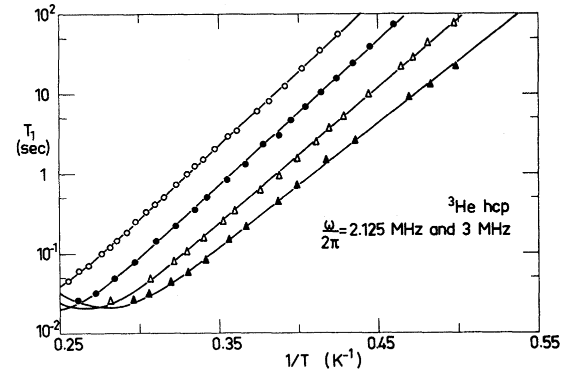

FIG. 3. Temperature dependence of the nuclear-spin-lattice relaxation times in hcp ³He (low-field data). ○, 17.63 cm³/mole; ●, 17.81 cm³/mole; △, 18.07 cm³/mole; ▲, 18.34 cm³/mole. Data at 17.63 cm³/mole were taken at $\omega/2\pi = 3$ MHz and the remainder at 2.125 MHz.

For the hcp phase, the activation energy W is definitely larger than for bcc and the preexponential factor τ_0 clearly shorter. In order to compare our results with the only other available experimental results related to vacancy motion in the hcp phase, we analyzed the data published by Reich[5] for $V = 18.82$ cm³ and at 5.224 MHz in the same manner as we analyze our data. As shown in Table I, Reich's values are reasonably

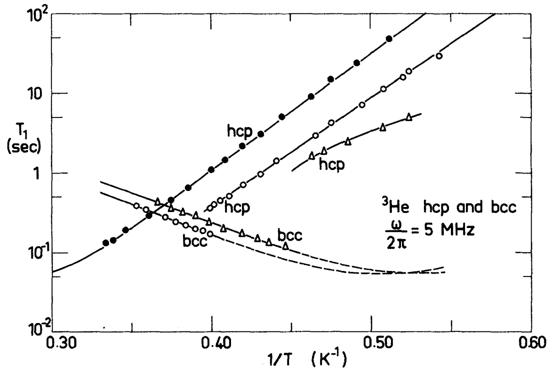

FIG. 4. Temperature dependence of the nuclear-spin-lattice relaxation times in hcp and bcc ³He in the region of the phase transition. ●, 18.95 cm³/mole; ○, 19.24 cm³/mole, phase transition at 2.45 K; △, 19.46 cm³/mole, phase transition at 2.25 K; (curvature of $\log T_1$ in the hcp phase is associated with the onset of Zeeman-exchange relaxation).

close to ours. τ_0 is roughly ten times shorter for hcp than for bcc. Since it is difficult to understand why the tunneling frequency is larger in hcp than in bcc, it is quite possible that, in hcp, the motion of vacancies is that of a classical jump over a barrier of height Φ_m. In that case we can measure the sum $W = \Phi + \Phi_m$ only by means of NMR and it is quite natural that the jump frequency of the vacancy in some thermally excited state, proportional to $1/\tau_0$, is larger than the tunneling frequency ω_V in the ground state. Near the transition molar volume an order of magnitude for the barrier Φ_m might be given by the discontinuity in the observed activation energies, which is shown in Fig. 5 and is of the order of 13 K.

We conclude this section with a remark about the thermalization of vacancies. If we cool the crystal a vacancy has to move somewhere to become annihilated if the thermal equilibrium number is to be obtained. Suppose it has to move to the surface as a well-behaved Schottky defect. This requires a thermalization time which is roughly

$$T_{\text{th}} \simeq \tau (l/a)^2 ,$$

where a is the previously defined lattice parameter and l is a characteristic length of the crystal. If $l \simeq 3$ mm, $\tau \simeq 2\times10^{-11}$ sec, $T_{\text{th}} \simeq 2000$ sec. Suppose we have a crystal at temperature T_i and we cool it rapidly to T_f. The number of vacancies will decrease with a time constant T_{th} and it will reach the final concentration within, say, 10% after time

$$t = T_{\text{th}} \left[\ln 10 + \ln\left(\exp\{\Phi[(1/T_f) - (1/T_i)]\} - 1 \right) \right] .$$

Taking $T_{\text{th}} = 2000$ sec, $\Phi = 14.5$ K, $1/T_i = 0.8$, $1/T_f = 0.7$, this time is of the order of 2 h. We have never observed such long response times for the relaxation time which is proportional to the vacancy concentration, so we conclude that $T_{\text{th}} \ll 2000$ sec and that the vacancies are not excited at the surface but on some dislocation lines. This has been postulated to account for the trapping of negative ions in solid ^{4}He,[21] and might also be relevant in solid ^{3}He, where some anomalous relaxation times have been observed below 0.4 K.[28]

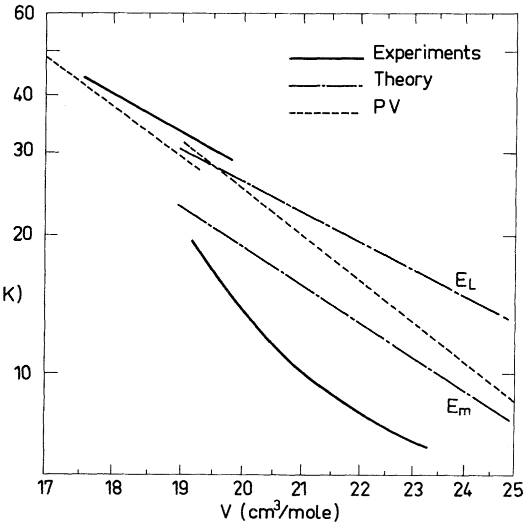

FIG. 5. Characteristic energies E as a function of molar volume. Solid curves are reproduced from Fig. 2. The theoretical curves are those of Hetherington (Ref. 1), where E_L and E_m represent the energy of a localized vacancy and the lower edge of the band of vacancy energies, respectively. The values of PV are taken from the data of Grilly (Ref. 24).

V. DISCUSSION

For the bcc lattice we find a tunneling frequency $\omega_V = (5.2\tau)^{-1} \simeq 0.5\times10^{10}$ sec^{-1} with an accuracy which is rather limited. The experimental inaccuracy accounts for the scatter of the values of τ_0 appearing in Table I. The corresponding vacancy-induced spin-diffusion constant would be $D = D_0 x$, where $D_0 = a^2/6\tau \simeq 0.5\times10^{-5}$ cm^2 sec^{-1}. This value is somewhat smaller than the spin-diffusion constant measured directly by Reich.[5] Our tunneling frequency in the bcc phase is roughly independent of the molar volume, a feature which is in agreement with the predictions of Hetherington.[1] Quantitatively there is nevertheless a disagreement. If we take the results of Brinkman and Rice[19] with our value for ω_V, Eq. (10) gives a vacancy bandwidth of 0.4 K, as opposed to a theoretical prediction of 12 K by Hetherington.[1] On the other hand, if we crudely estimate the tunneling frequency ω_V with "undistorted" ground-state single-particle wave functions,

$$\varphi_R(\vec{x}) = \pi^{-3/4} \alpha^{3/2} \exp\left[-\tfrac{1}{2}\alpha^2 (\vec{x} - \vec{R})^2\right] , \qquad (16)$$

we find[29]

$$\omega_V = (\hbar / m\sqrt{\pi}\,) \alpha^3 a\, e^{-(1/4)\alpha^2 a^2} . \qquad (17)$$

Using the parameter α^2 of Sarkissian's thesis[30] one finds for $V = 22$ cm^3, $\alpha^2 = 1.69$ A^{-2}, $\omega_V = 3.7\times10^{10}$ sec^{-1}, a value about seven times larger than ours which decreases with decreasing molar volume.

As far as the hcp lattice is concerned, as we pointed out in Sec. IV, NMR is at present the only technique sensitive to the existence of vacancies in the hcp lattice, and we cannot make the statement that we have observed the tunneling of vacancies. We are not aware of any published theoretical predictions for tunneling in the hcp lattice. If we scale Eq. (9), written for the bcc lattice, by the number of nearest neighbors in the hcp lattice, the preexponential factor for the jump time would be

$$\tau = (12/8A\omega_V)^{-1} . \tag{18}$$

Using the measured preexponential factor given in Table I for $V = 18.95$ cm^3/mole, this yields a value $\omega_V = 0.5 \times 10^{11}$ sec^{-1} for the tunneling frequency. Since this molar volume is rather close to the bcc-hcp transition line, it is hard to understand how ω_V could be considerably larger in a close-packed structure than in the bcc lattice. The other possibility raised in Sec. IV is that the motion of vacancies could be that of a classical jump in the hcp lattice.

If the x-ray diffraction measurements could be extended to the hcp phase of ^{3}He, this would provide us with complementary information capable of solving this dilemma.

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