Properties of solid $^3$He inclusions embedded in crystalline $^4$He matrix at ultralow temperatures


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A study is made of the kinetic properties of the quantum systems formed in dilute solid mixtures of $^3$He in $^4$He at ultralow temperatures as a result of the first-order phase transition known as phase separation. The system is a crystalline matrix of almost pure $^4$He in which small solid inclusions of almost pure $^3$He are embedded. Data on the inclusion growth kinetics, which is governed by diffusion processes in the matrix, are obtained using precise pressure measurements at constant volume. It is shown that impurion quantum diffusion is the main process causing the inclusion growth at $T > 100$ mK. At lower temperatures a strong suppression of quantum diffusion is discovered. This suppression can be associated with the elastic strains induced by the large difference in molar volume between the matrix and inclusions. The magnetic relaxation processes in such two-phase crystals are also investigated using a pulsed NMR technique. The spin-lattice and spin-spin relaxation in the inclusions are found to be practically independent of temperature. This can be described by exchange processes associated with the $^3$He tunnel motion. The values of the relaxation times are in good agreement with the corresponding times for pure bulk $^3$He. In contrast with the case of pure solid $^3$He, the exchange plateau region extends down to lower temperatures. The nuclear magnetic relaxation in the matrix can be described by the Torrey model, which is based on $^3$He-$^4$He tunnel exchange. The concentration dependence of the relaxation times coincides with that observed for homogeneous dilute mixtures of $^3$He in $^4$He.

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1. Introduction

Helium isotopes and their solid mixtures are the most typical examples of the not numerous but very interesting (in their scientific aspect) class of substances, called quantum crystals (QCs). The influence of the zero-point motions of the atoms on the properties of QCs is a characteristic feature of these objects which becomes decisive at rather low temperatures.

The zero-point motions are manifested especially expressively in the behavior of impurities and defects inside QCs. As has been shown by Andreev and Lifshits [11], the point defects in this case delocalize and turn into quasiparticles (QPs), which can move inside the crystal almost freely. This gives rise to the quantum diffusion (QD) phenomenon, which is characterized by a very unusual nature of the diffusive motion. The diffusion coefficient (DC) is either independent of temperature, if the motion of the QPs is restricted by their mutual collisions, or even rises with cooling, if the interaction with phonons plays the main role. Such regularities have been reliably established for $^3$He impurities in hcp $^4$He crystals (see, for example, Ref. 2) using NMR measurements of spin diffusion (SD). The main parameters characterizing the QD of impurity QPs in this system were also found.

However, a number of peculiarities of the diffusive motion could not be studied in the SD measurements. In particular, the regularities of mutual mass diffusion realized in the presence of a finite concentration gradient still remain unclear. In this case, one would expect a significant change of the role of mutual QP collisions, which may be effective only in proportion to the $U$-process probability. In ordinary classic crystals the self-diffusion coefficient is usually measured using the radioactive isotope technique, which can not be implemented in solid helium. Nonetheless, its general idea (measurement of
the penetration rate of an impurity into a matrix) can be used even in this case. Using the known DC values for solid helium, one can estimate the distance to which the impurity would penetrate for a reasonable duration of the experiment. For a duration of several hours (\( \sim 10^4 \) s) this distance is about \( 10^{-2} \) cm for mixtures with a \( ^3 \)He concentration of \( 10^{-2} - 10^{-3} \), where the DC is \( 10^{-5} - 10^{-8} \) cm\(^2\)/s. Measurement of the impurity concentration distribution in a helium crystal at such distances is a rather complicated problem. NMR tomography, for example, allows one to measure only DCs \( > 10^{-7} \) cm\(^2\)/s [3,4].

From this point of view the study of another peculiar phenomenon in QCs, the so-called isotopic phase separation at low temperatures, is very promising. As has been established in experiment [5], homogeneous mixtures of the helium isotopes separate into two phases below 0.38 K. If the initial mixture is dilute enough, a system consisting of isotopic impurity inclusions in a matrix of the other isotope is formed at \( T \to 0 \). Such a system is rather convenient for investigating mass diffusion in helium crystals. Experiments [6] have given an inclusion size of about \( 10^{-4} \) cm at low temperatures. Therefore, the distance between inclusions at an initial concentration of \( 10^{-2} \) is about \( 10^{-3} \) cm. A change in temperature of the phase-separated mixtures causes a change in the equilibrium concentration in both the matrix and inclusions formed, so it is accompanied by diffusive mass transfer. In accordance with the estimate given above, the diffusion paths are such that characteristic times of variations in the concentration are about \( 10^2 - 10^3 \) s, well acceptable for measurement. It should be noted that in this case one can determine in situ the DC of \( ^4 \)He, which cannot be measured by the NMR method at all and on which reliable data are now lacking.

The system under consideration is also interesting from the standpoint of clearing up another poorly known aspect of QD, namely the diffusive motion under conditions of a stressed state of the sample. The point is that a phase with a molar volume significantly different from that of the matrix appears upon phase separation. As a result, strains arise near the inclusions and may influence the diffusive mobility of QPs. The influence of strains on diffusion has not been adequately studied in the classic case. Besides, an additional mechanism involving the energy level shift between neighboring lattice sites appears in QCs. This leads to a decrease of the probability of tunneling, a breakdown of the coherent motion of QPs, and a corresponding decrease of DC.

The quantum nature of helium crystals is clearly manifested in their magnetic properties, too. The large amplitude of the helium atom zero-point motion gives rise to a strong exchange interaction, which causes a tunneling atom motion and may change the magnetic relaxation processes. This problem has been investigated in detail only in monophase crystals, namely solid \( ^3 \)He and homogeneous \( ^3 \)He–\( ^4 \)He mixtures [7–9]. As to the above mentioned two-phase crystal, consisting of \( ^3 \)He inclusions in a \( ^4 \)He matrix, such investigations have just started [6,10]. The matrix of almost pure \( ^4 \)He may change significantly the nuclear magnetic relaxation at ultralow temperatures. On the one hand, being chemically inactive and nonmagnetic, the matrix excludes the familiar wall mechanisms of relaxation. On the other hand, the transition region between the hep matrix and the bcc inclusions is supposed to contain a great number of defects, which may be collectors for magnetic excitations of the Zeeman reservoir [7]. We present the experimental data both on the phase separation kinetics of solid \( ^3 \)He–\( ^4 \)He mixtures and the corresponding diffusion processes and on the magnetic properties of solid \( ^3 \)He inclusions in the \( ^4 \)He matrix in a millikelvin temperature region.

2. Formation kinetics of \(^3\)He–\(^4\)He mixture two-phase crystal and features of \(^3\)He impurity mass diffusion

The phase separation kinetics of solid \( ^3 \)He–\( ^4 \)He mixtures was studied by precise pressure measurements at a constant volume. The method is based on the excess molar volume \( V_E \) emerging during the phase separation of the two-component mixtures, and for solid helium isotopes it is [11]

\[
V_E = 0.4x(1-x) \text{[cm}^3\text{/mol]}
\]

where \( x \) is the concentration of the mixture.

As the experiments were carried out at a constant volume, the phase transition produces a change in pressure \( \Delta P \), which is proportional to \( V_E \) and, for small concentrations, to the change in the concentration \( \Delta x \).

The cell is a flat cylinder 9 mm in diameter and 1.5 mm in height, described in detail in Ref. 12. The samples with an initial \( ^3 \)He concentration \( x_0 \) of \( \approx 2.05\% \) were grown using the capillary blocking technique. The annealing of the crystals was carried out for a day at a temperature close to the melting curve. The sample temperature was cycled many times.
times in the two-phase region after annealing. As a result of this procedure, the crystal quality was improved, namely, the phase separation time constant became reproducible and the crystal pressure decreased [13]. The measurements were made in a temperature range of 50–300 mK with a molar volume of 20.27 cm³/mol, corresponding to a pressure of 35.99 bar at the phase separation temperature $T_{ps}$.

The phase separation was initiated by the step-by-step cooling of the solid $^3$He–$^4$He mixture below $T_{ps}$, followed by a long temperature stabilization. The equilibrium pressure in the crystal established by the exponential law

$$P(t) = P_f - (P_f - P_i) \exp \left(-\frac{t}{\tau}\right),$$

where $\tau$ is the characteristic time governing the kinetics of phase separation after cooling by $\Delta T$; $P_i$ is the initial pressure in the sample, and $P_f$ is the final equilibrium pressure for the given temperature.

Figure 1 shows the time dependence of the relative change in pressure on a logarithmic scale for each cooling step. According to (1), the slope of the lines corresponds to the time constant $\tau$. As is clearly evident from Fig. 1, the characteristic times of phase separation decrease with temperature (lines 1–4), but they start to increase (lines 5–7) below some temperature ($= 110$ mK). The time constants $\tau$ determined in such a way can be associated with the effective diffusion coefficient, which provides a $^3$He atom transfer to the new phase inclusions. The average size of the $^3$He inclusions was measured most reliably by the confined diffusion NMR technique [6] and is about 4.5 μm.

The relation between $D_{\text{eff}}$ and $\tau$ was found by solving the corresponding diffusion problem [14].

![Fig. 1](image1.png)

**Fig. 1.** The time dependence of the relative change in pressure for a sample with a molar volume of 20.27 cm³/mol on a logarithmic scale. Solid lines are fits to (2) for different final temperatures, mK: 151 (1); 136 (2); 121 (3); 105 (4); 96 (5); 80.3 (6); 61.6 (7).

The estimated values of mass diffusion coefficient is worthwhile to compare with the self-diffusion coefficient of impurities $D_s$, measured earlier in NMR experiments for solid $^3$He–$^4$He mixtures of the same concentration by the spin-echo method [15]. In Fig. 2 we present the ratio of $D_{\text{eff}}/D_s$ as a function of temperature (concentration). As the measurements were carried out along the phase separation curve, a mutual conformity between temperature and concentration takes place. One can see that $D_{\text{eff}}$ and $D_s$ practically coincide at high temperatures. This means, that the quantum diffusion under such conditions is the main mechanism which provides the $^3$He inclusion growth in the $^4$He matrix. However, as the temperature goes down, $D_{\text{eff}}$ becomes much less than $D_s$, and the difference is more than two orders of magnitude at lowest temperatures. As follows from Fig. 2, the impurity quantum diffusion from the matrix to the inclusions is strongly suppressed in the low-temperature region. The most probable reason for this effect is the influence on diffusion of the elastic fields that appear in the matrix during nucleation and growth of new phase inclusions with a molar volume much higher than that of the matrix. Under such conditions the diffusion flow can be written as follows [16]:

$$j = -\frac{Dx}{\omega} \left(\frac{\nabla x + \nabla U}{kT}\right),$$

**Fig. 2.** The ratio $D_{\text{eff}}/D_s$ vs temperature (concentration) for a crystal with a molar volume of 20.27 cm³/mol.
where \( v \) is the atomic volume; \( \nabla v \) is the concentration gradient, and \( \nabla U \) is the potential gradient characterizing the inhomogeneous stress field. A significant decrease of mass transfer may take place at low temperatures on the condition that \( \nabla v \) and \( \nabla U \) have opposite directions and comparable values. The elastic force gradient appearing during the solid \(^3\)He inclusion growth in the \(^4\)He matrix can strongly influence the QD, slowing it down through either the action of a direct force or an energy level shift of neighboring lattice sites.

Thus the \(^3\)He mass transfer in the system formed during phase separation and consisting of \(^3\)He inclusions in a solid \(^4\)He matrix differs significantly from that in a homogeneous mixture. Further experimental and theoretical work is needed to explain the facts described.

3. Magnetic relaxation in phase separated dilute \(^3\)He–\(^4\)He mixture

Cylindrical samples of solid \(^3\)He–\(^4\)He mixtures, 4 mm in diameter and 20 mm long, were grown from an initial gaseous mixture containing 3.18\% \(^3\)He by the capillary blocking method in an experimental cell [17] cooled with a nuclear demagnetization refrigerator. After annealing for a day near the melting temperature, the molar volume of the samples was \((20.3\pm0.05)\ \text{cm}^3/\text{mol}\). The 250 kHz pulsed NMR spectrometer was used to measure the spin–lattice \(T_{1d}\), and spin–spin \(T_{2s}\) relaxation times and spin diffusion coefficient \(D_s\).

The difference between spin–lattice relaxation times in the matrix, with a low \(^3\)He concentration, \(T_{1d}^d\), and in the concentrated dispersed phase, \(T_{1c}^c\), made it possible to separate the NMR signals from the two phases after phase separation. Consequently, the spin–lattice and spin–spin relaxation times were measured in both the matrix and inclusions of concentrated \(^3\)He.

The temperature dependences of \(T_1\) and \(T_2\) are shown in Fig. 3. The times \(T_{1c}^c\) and \(T_{2c}^c\) for the concentrated phase inclusions are seen to be practically independent of temperature. This allows us to propose that in this case the main relaxation mechanism is connected with the Zeeman-tunnel interaction. This is supported by the coincidence of our experimental \(T_{1c}^c\) value of 200 ms with the theoretical results given in Ref. 7. As in this experiment the Larmor frequency is much less than the tunnel exchange frequency \(\omega_E\), the times \(T_1^c\) and \(T_2^c\) in solid \(^3\)He almost coincide in the «exchange plateau» region and are given as follows [7]:

\[
(T_{1c}^c)^{-1} = (T_{2c}^c)^{-1} = \frac{10}{3} \left( \frac{\pi}{2} \right)^{1/2} \frac{M_2}{\omega_E},
\]

where \(M_2\) is the second Van Vleck moment.

Besides, the obtained values of \(T_{1c}^c\) are equal to the known ones for bulk solid \(^3\)He in the «exchange plateau» region under the same conditions [7]. The main difference is that the exchange plateau for solid bulk \(^3\)He exists at temperatures above 0.25 K, but at lower temperatures a sharp increase of \(T_1^c\) occurs. This increase is due to a weakening of the bond between the exchange reservoir and the lattice. This bond in bulk samples is provided by both vacancion and impurion relaxation mechanisms [7]. Meanwhile, temperature independence of \(T_{1c}^c\) for the \(^3\)He inclusions in the \(^4\)He matrix takes place over the temperature region in question down to 1.5 mK.

The disagreement may be due to the small inclusion sizes and a considerable amount of \(^4\)He in the inclusions, at least near \(T_{1c}^c\). However, the mechanism that provides the strong bond between the exchange reservoir and the lattice under such conditions is unclear.

As is clearly evident from Fig. 3, \(T_{2c}^c\) is temperature independent in the region 50–200 mK and equals \((0.21\pm0.02)\ s\). The temperature independence of \(T_{2c}^c\) and its coincidence with both the experimental values [7] of \(T_2^c\) for bulk pure \(^3\)He and the calculations according to (4) allows us to suppose that the spin–spin relaxation mechanism is determined by the \(^3\)He–\(^4\)He tunneling exchange frequency, independent of temperature. Nevertheless, the \(T_{2c}^c\) time tends to decrease down to 0.15 s below \(50\) mK (see Fig. 3).

The decrease of \(T_2\) is usually considered as being due to a reduction in \(D_s\) [18]. Our measurements show that \(D_s\) is \((7\pm2\cdot10^{-8})\ \text{cm}^2/s\) in the inclusions.

Fig. 3. Temperature dependence of the spin–lattice (■—\(T_{1d}^d\), △—\(T_{1c}^c\)) and spin–spin (□—\(T_{2d}^d\), △—\(T_{2c}^c\)) relaxation times.
Thus all the data obtained in this study ($T_1$, $T_2$, and $D_s$) testify to the similarity of the properties of separated phases and those of bulk solid helium. The reasons for the extending of the $T_1$ «exchange plateau» to ultralow temperatures and the decrease in $T_2$ at $T < 50$ mK are unclear.