

Properties of solid ^3He inclusions embedded in crystalline ^4He 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 ^3He in ^4He 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 ^4He in which small solid inclusions of almost pure ^3He 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 impuriton 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 ^3He tunnel motion. The values of the relaxation times are in good agreement with the corresponding times for pure bulk ^3He . In contrast with the case of pure solid ^3He , 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 ^3He – ^4He tunnel exchange. The concentration dependence of the relaxation times coincides with that observed for homogeneous dilute mixtures of ^3He in ^4He .

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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 [1], 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 tempera-

ture, 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 ^3He impurities in hcp ^4He 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 ^3He concentration of 10^{-2} – 10^{-3} , where the DC is 10^{-9} – 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 $T \rightarrow 0$. 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 ^4He , 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 monophasic crystals, namely solid ^3He and homogeneous ^3He – ^4He mixtures [7–9]. As to the above mentioned two-phase crystal, consisting of ^3He inclusions in a ^4He matrix, such investigations have just started [6,10]. The matrix of almost pure ^4He 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 hcp 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 ^3He – ^4He mixtures and the corresponding diffusion processes and on the magnetic properties of solid ^3He inclusions in the ^4He matrix in a millikelvin temperature region.

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

The phase separation kinetics of solid ^3He – ^4He 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]

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

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 ΔP , which is proportional to V_E and, for small concentrations, to the change in the concentration Δx .

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 ^3He 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 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 ³He–⁴He mixture below T_{ps} , followed by a long temperature stabilization. The equilibrium pressure in the crystal established by the exponential law

$$P(t) = P_f - (P_f - P_i) \exp(-t/\tau), \quad (2)$$

where τ is the characteristic time governing the kinetics of phase separation after cooling by ΔT ; 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 τ . 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 τ determined in such a way can be associated with the effective diffusion coefficient, which provides a ³He atom transfer to the new phase inclusions. The average size of the ³He inclusions was measured most reliably by the confined diffusion NMR technique [6] and is about 4.5 μ m.

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

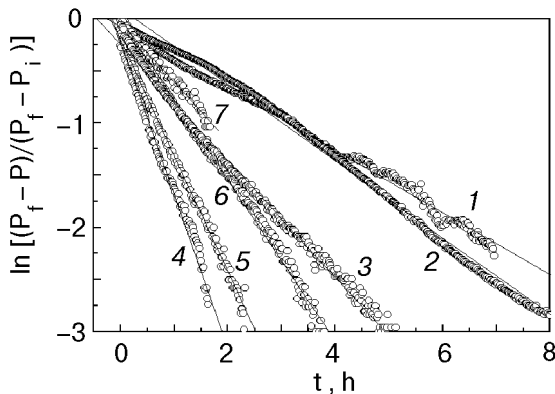


Fig. 1. The time dependence of the relative change in pressure for a sample with a molar volume of 20.27 cm³/mol on a logarithmic scale. Solid lines are fits to (2) for different final temperatures, mK: 151 (1); 136 (2); 121 (3); 105 (4); 96 (5); 80.3 (6); 61.6 (7).

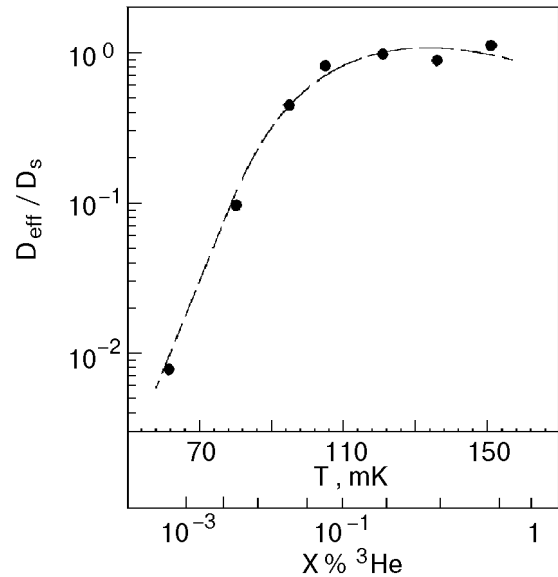


Fig. 2. The ratio D_{eff}/D_s vs temperature (concentration) for a crystal with a molar volume of 20.27 cm³/mol.

The estimated values of mass diffusion coefficient is worthwhile to compare with the self-diffusion coefficient of impuritons D_s , measured earlier in NMR experiments for solid ³He–⁴He mixtures of the same concentration by the spin-echo method [15]. In Fig. 2 we present the ratio of D_{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_{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 ³He inclusion growth in the ⁴He matrix. However, as the temperature goes down, D_{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 impuriton 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]:

$$j = -\frac{Dx}{w} \left(\frac{\nabla x}{x} + \frac{\nabla U}{kT} \right), \quad (3)$$

where ω is the atomic volume; ∇x is the concentration gradient, and ∇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 ∇x and ∇U have opposite directions and comparable values. The elastic force gradient appearing during the solid ${}^3\text{He}$ inclusion growth in the ${}^4\text{He}$ 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 ${}^3\text{He}$ mass transfer in the system formed during phase separation and consisting of ${}^3\text{He}$ inclusions in a solid ${}^4\text{He}$ 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 ${}^3\text{He}$ - ${}^4\text{He}$ mixture

Cylindrical samples of solid ${}^3\text{He}$ - ${}^4\text{He}$ mixtures, 4 mm in diameter and 20 mm long, were grown from an initial gaseous mixture containing 3.18% ${}^3\text{He}$ 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 $(20.3 \pm 0.05) \text{ cm}^3/\text{mol}$. The 250 kHz pulsed NMR spectrometer was used to measure the spin-lattice (T_1) and spin-spin (T_2) relaxation times and spin diffusion coefficient D_s .

The difference between spin-lattice relaxation times in the matrix, with a low ${}^3\text{He}$ concentration, T_1^d , and in the concentrated dispersed phase, T_1^c , made it possible to separate the NMR signals from the two phases after phase separation. Conse-

quently, the spin-lattice and spin-spin relaxation times were measured in both the matrix and inclusions of concentrated ${}^3\text{He}$.

The temperature dependences of T_1 and T_2 are shown in Fig. 3. The times T_1^c and T_2^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_1^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 ω_E , the times T_1 and T_2 in solid ${}^3\text{He}$ almost coincide in the «exchange plateau» region and are given as follows [7]:

$$(T_1^c)^{-1} \approx (T_2^c)^{-1} \approx \frac{10}{3} \left(\frac{\pi}{2} \right)^{1/2} \frac{M_2}{\omega_E}, \quad (4)$$

where M_2 is the second Van Vleck moment.

Besides, the obtained values of T_1^c are equal to the known ones for bulk solid ${}^3\text{He}$ in the «exchange plateau» region under the same conditions [7]. The main difference is that the exchange plateau for solid bulk ${}^3\text{He}$ exists at temperatures above 0.25 K, but at lower temperatures a sharp increase of T_1 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 vacancy and impurity relaxation mechanisms [7]. Meanwhile, temperature independence of T_1^c for the ${}^3\text{He}$ inclusions in the ${}^4\text{He}$ 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 ${}^4\text{He}$ in the inclusions, at least near T_{ps} . 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_2^c is temperature independent in the region 50–200 mK and equals $(0.21 \pm 0.02) \text{ s}$. The temperature independence of T_2^c and its coincidence with both the experimental values [7] of T_2 for bulk pure ${}^3\text{He}$ and the calculations according to (4) allows us to suppose that the spin-spin relaxation mechanism is determined by the ${}^3\text{He}$ - ${}^4\text{He}$ tunneling exchange frequency, independent of temperature. Nevertheless, the T_2^c time tends to decrease down to 0.15 s below $\sim 50 \text{ mK}$ (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 $(7 \pm 2 \cdot 10^{-8}) \text{ cm}^2/\text{s}$ in the inclusions

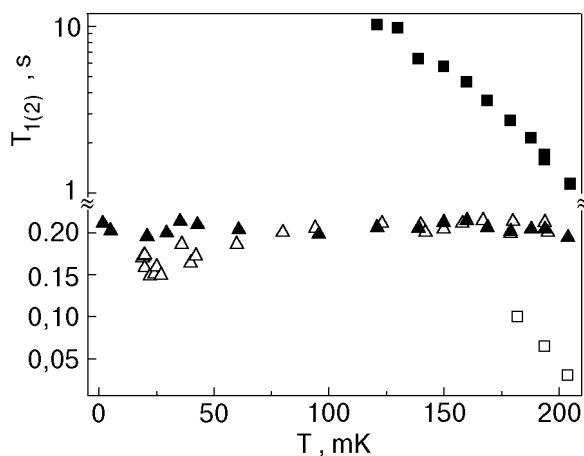


Fig. 3. Temperature dependence of the spin-lattice ($\blacksquare - T_1^d$, $\blacktriangle - T_1^c$) and spin-spin ($\square - T_2^d$, $\triangle - T_2^c$) relaxation times.

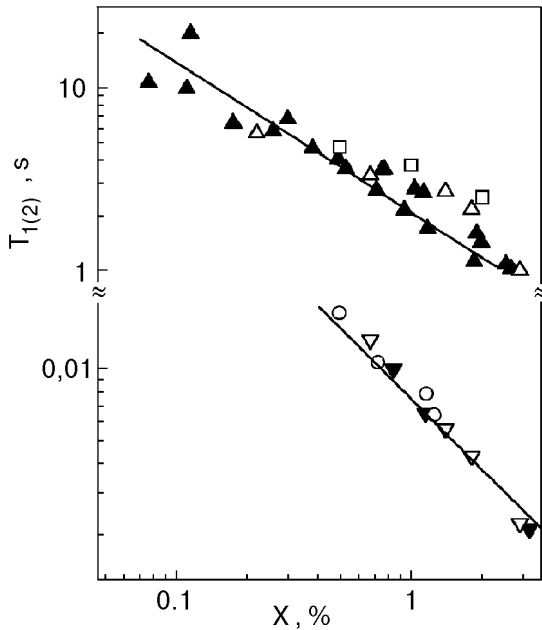


Fig. 4. Concentration dependence of the spin-lattice T_1 (\blacktriangle) and spin-spin T_2 (\blacktriangledown) relaxation times in the dilute hcp matrix. The experimental results obtained in Ref. 8 (\square , \blacktriangledown), Ref. 9 (\triangle), and Ref. 6 (\circ), were normalized to our experimental conditions. The solid lines correspond to dependences $T_1 \sim x^{-0.88}$ and $T_2 \sim x^{-1}$.

down to 1.5 mK. This value of D_s is close to that for pure bulk ^3He of the same density [7].

As expected, in the hcp matrix both the spin-spin relaxation time T_2^d and T_1^d depend on temperature in proportion to the ^3He concentration change, which is determined by the phase separation diagram.

The concentration dependences of T_1 and T_2 are shown in Fig. 4 alongside the well-known experimental data for homogeneous solid ^3He - ^4He mixtures under the same conditions. All the experimental data can be explained, solely by a dependence which conforms with the Torrey nuclear relaxation model [19]. This implies that the main mechanism of spin-spin and spin-lattice relaxation is due to the ^3He - ^4He tunneling exchange.

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.

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