

# Spin relaxation of atoms during quantum diffusion in a crystal

N. V. Prokof'ev and G. V. Shlyapnikov

*I. V. Kurchatov Institute of Atomic Energy, Moscow*

(Submitted 15 April 1987)

Zh. Eksp. Teor. Fiz. **93**, 2109–2120 (December 1987)

The spin relaxation of impurity atoms in a crystal is studied under conditions such that quantum tunneling diffusion of these atoms dominates. In a strong magnetic field, with  $\omega_0 \gg \Delta$ ,  $\xi_{\max}$  ( $\omega_0$  is the Zeeman transition energy,  $\Delta$  is the width of the coherent-motion band, and  $\xi_{\max}$  is the maximum shift of the energy levels between neighboring positions of the atom in the nonideal lattice), the ordinary phonon relaxation mechanism operates. In this case, the spatial profile of the interdiffusion coefficient of the impurity atoms can be determined from their relaxation time. In the opposite limit, with  $\omega_0 \ll \Delta$ , the Bloembergen phononless relaxation mechanism operates, with conversion of the energy  $\omega_0$  into the energy of band motion. The fact that there are regions of both band and diffusive motion distinguishes this problem substantially from the conventional magnetic-resonance problems. At intermediate values of the magnetic field, a nontrivial phononless relaxation mechanism operates: A spin flip occurs directly during the tunneling of an atom into a neighboring cell. In this case the energy-level shift  $\xi$  is offset by a change in the Zeeman energy  $\omega_0$ . The theoretical results are used to analyze experimental data on the spin relaxation of H atoms in an H<sub>2</sub> crystal and of He<sup>3</sup> atoms in a He<sup>4</sup> crystal.

## 1. INTRODUCTION

The quantum tunneling diffusion of impurity particles in a crystal has become the subject of active theoretical and experimental research. This effect is seen most vividly in such systems as atomic hydrogen in an H<sub>2</sub> matrix<sup>1,2</sup> and a solid solution of He<sup>3</sup> in He<sup>4</sup> (Refs. 3–5). The quantum nature of the diffusion has a decisive effect on the kinetics of the spin relaxation of impurity particles since the probability for these processes increases sharply when particles approach to within small distances of each other. As a result, it becomes possible to bring out many aspects of quantum diffusion from data on the relaxation kinetics.

In this paper we report a study of the most effective spin-relaxation mechanisms in the quantum diffusion of H atoms in an H<sub>2</sub> matrix and of He<sup>3</sup> atoms in a He<sup>4</sup> crystal. The physical picture of spin relaxation in this case is determined by three parameters: the Zeeman transition energy  $\omega_0$ , the width of the coherent-motion band  $\Delta$ , and the maximum shift of the energy levels between neighboring positions of an atom in the nonideal lattice,  $\xi_{\max}$ . Under the conditions

$$\omega_0 \gg \Delta, \xi_{\max} \quad (1.1)$$

energy conservation requires the emission or absorption of phonons as a result of the relaxation. The electron spin of a hydrogen atom in a H<sub>2</sub> matrix relaxes in a strong magnetic field by a phonon mechanism. At a sufficiently high concentration of H atoms, the interaction of these atoms with each other plays a dominant role. A specific feature of quantum diffusion is seen here, in the fact that the local interdiffusion coefficient becomes dependent on the distance between atoms which are converging on each other. This dependence can be established by comparing theoretical and experimental data (Sec. 2).

In a weak magnetic field, condition (1.1) no longer holds, and phononless mechanisms for spin relaxation become possible. A situation of this sort arises for the electron spin of a hydrogen atom in a para-H<sub>2</sub> crystal (with a small admixture of ortho-H<sub>2</sub>) in a field  $H \sim 0.1$ –1 T. Here the con-

dition  $\omega_0 > \Delta$  holds, and a nontrivial phononless relaxation mechanism operates: Because of the level shifts ( $\xi = \omega_0$ ) of the hydrogen atom near an orthomolecule, the spin flip may occur directly during the tunneling of the atom into a neighboring cell. The level shift is offset by a change in the Zeeman energy in this process. Similar shifts arise from an anisotropic interaction of an atom with an orthomolecule and by virtue of the large number of possible positions of an atom near an orthomolecule. They also result from the uncontrollable broadening which results from the interaction with other defects. They form a quasicontinuous band of width  $\sim 1$  K.

Under the condition  $\omega_0 < \Delta$ , the Bloembergen phononless relaxation mechanism (Ref. 6, for example) operates. According to this mechanism, the spin is flipped as a result of fluctuations in the dipole-dipole interaction at the frequencies  $\omega_0$  and  $2\omega_0$  which arise as particles move with respect to each other. In this case, the Zeeman energy  $\omega_0$  can be offset by a change in the energy of the band motion. A situation of this sort occurs in particular for He<sup>3</sup> atoms in a He<sup>4</sup> crystal in a weak magnetic field. A specific feature which distinguishes this system from the conventional magnetic-resonance systems is the presence of regions of both diffusive and band motions. The analysis in Sec. 4 explains the experimentally observed features in the behavior of the transverse relaxation time  $T_2$  as a function of the temperature and the He<sup>3</sup> concentration. It predicts a nontrivial behavior of the longitudinal relaxation time  $T_1$  at low temperatures,  $T \lesssim 0.5$  K, and also at concentrations  $x \gtrsim 10^{-2}$ .

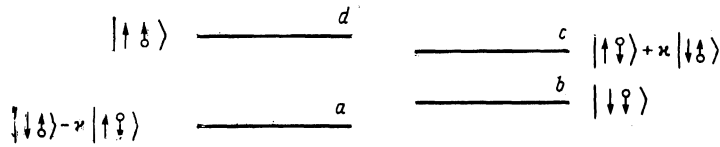
## 2. PHONON MECHANISM FOR THE SPIN RELAXATION OF HYDROGEN ATOMS IN A H<sub>2</sub> MATRIX

For a hydrogen atom in an H<sub>2</sub> matrix the width of the coherent-motion band is  $\Delta \sim (10^{-1} - 10^{-3})$  K, according to current estimates.<sup>7,8</sup> The scale value of the level shift which occurs as two atoms converge on each other, or when the ortho-para composition of the molecules surrounding one atom changes, is less than  $\xi_{\max} \sim 1$  K. Condition (1) thus holds for the electron spin in a strong magnetic field ( $H \sim 10$

$T, \omega_0 \approx 2\mu_B H \sim 10$  K), and the spin relaxation is of a phonon nature. At temperatures  $T \ll \omega_0$ , which definitely correspond to a region of quantum diffusion, two-phonon and multi-phonon processes are ineffective, and the spin relaxation is

accordingly accompanied by the emission or absorption of one phonon with an energy  $\omega_0$ .

In a strong magnetic field, the system of spin levels of the hydrogen atom is



Here the symbols  $\uparrow$  and  $\downarrow$  correspond to electron and nuclear spins. The quantity  $\kappa$  is equal to  $A/4\mu_B H \ll 1$ , where  $A$  is the hyperfine-interaction constant. Two types of electron transitions are possible: allowed electron transitions  $da$  and  $cb$  and the forbidden transition  $ca$ , whose amplitude differs from zero to the extent that the small parameter  $\kappa$  does.

Both of these transitions are due primarily to the dipole-dipole spin interaction of H atoms with each other and with orthomolecules:

$$\begin{aligned} (\hat{V}_d)_{ij} &= \frac{(\hat{\mu}_i \hat{\mu}_j) \mathbf{R}_{ij}^2 - 3(\hat{\mu}_i \mathbf{R}_{ij})(\hat{\mu}_j \mathbf{R}_{ij})}{\mathbf{R}_{ij}^5} \\ &\equiv \frac{\mu_i \mu_j}{S_i S_j} \sum_{q=-2}^2 \frac{Y_2^q(\mathbf{n}_{ij}) S_{ij}^q}{R_{ij}^3}. \end{aligned} \quad (2.1)$$

Here  $\mathbf{R}_{ij}$  is the distance between particles;  $\mu_i, \mu_j, S_i, S_j$  are their magnetic moments and spins;  $Y_2^q$  are the spherical harmonics; and  $S_{ij}^q$  are irreducible tensor spin operators (Ref. 6, for example).

If the atomic density is sufficiently high, the time scale for the spin relaxation is determined by the interaction of atoms with each other and, correspondingly, by the competition between relaxation and diffusion processes. Since the diffusion is quantum-mechanical, the local interdiffusion coefficient of the atoms,  $D$ , may depend on the distance  $r$  between atoms which are approaching each other (Refs. 8 and 9).

Let us find the time scale  $T_{ca}$  for a forbidden transition under these conditions. We assume that we are dealing with a system which has atoms only in states  $c$  and  $a$  and that by virtue of the condition  $T \ll \omega_0$  the concentration satisfies  $x_c \ll x_a \approx x$ . We first calculate the probability for spin relaxation in the case in which the particles in states  $c$  and  $a$  are separated by a distance  $r$ . Expanding the interaction (2.1) in the relative displacements of the atoms from their equilibrium positions, and evaluating the matrix element in terms of phonon and spin variables, we find the following expression for the relaxation probability:

$$W(r) \approx \frac{3\kappa^2 \mu_B^4}{r^6} \frac{\omega_0^3}{M c_{\perp}^5} \Omega_0. \quad (2.2)$$

Here  $M$  is the mass of the hydrogen molecule,  $\Omega_0 \equiv a^3$  is the volume of a unit cell, and  $c_{\perp}$  is the transverse sound velocity (we are ignoring the process involving the emission of a longitudinal phonon, for which the sound velocity is twice as large).

In a system of randomly arranged particles, the particles are separated from each other for the most part by an average distance

$$\bar{R} \approx (\Omega_0/x)^{1/3}. \quad (2.3)$$

The quantity  $W$  in (2.2) is exceedingly small at such distances ( $x \lesssim 10^{-4}$ ). The possibility that the atoms will come close together substantially increases the relaxation probability. The relaxation occurs most effectively at distance at which the time scale of the diffusive motion of the particles with respect to each other,  $r^2/D(r)$ , becomes equal in order of magnitude to  $1/W(r)$ . It has been established experimentally that the time scale for the spin relaxation is much shorter than the time scale for the recombination of atoms into a molecule,<sup>2,10,11</sup> which is  $a^2/D(a)$ . This result means that the relaxation occurs over distances greater than one lattice constant. To determine  $T_{ca}$  in this case we need to examine the kinetic equation for the density matrix of a pair of particles, incorporating diffusion along with relaxation. This equation is

$$\partial f(\mathbf{r}, t)/\partial t = \text{div } 2D(\mathbf{r}) \nabla f(\mathbf{r}, t) - W(\mathbf{r})f(\mathbf{r}, t). \quad (2.4)$$

The function  $f(\mathbf{r}, t)$  gives the probability for finding particles  $c$  and  $a$  at a distance  $\mathbf{r}$  from each other, and  $2D(\mathbf{r})$  is the interdiffusion coefficient. In the limit of low atomic hydrogen concentration,  $x \ll 1$  (in practice,  $x \lesssim 10^{-4}$ ), we can use a quasisteady description, since the concentration of particles varies only slightly over the time required for the establishment of the particle profile. As a result we find the equation

$$2 \frac{1}{r^2} \frac{\partial}{\partial r} r^2 D(r) \frac{\partial f}{\partial r} \equiv W(r)f(r) \quad (2.5)$$

with the boundary condition

$$f(\infty) = x x_c(t). \quad (2.6)$$

Working from (2.5) and (2.6) in the standard way, we can find the flux of  $c$  particles in the direction of the  $a$  particles, which go into the state  $a$  as a result of the relaxation; correspondingly, we can find the transition time  $T_{ca}$ . For an arbitrary power law

$$D(r) = D(a)(r/a)^n, \quad n \geq 0 \quad (2.7)$$

we have

$$T_{ca}^{-1} \approx 4\pi x W(a) [D(a)/a^2 W(a)]^{3/(n+4)}. \quad (2.8)$$

According to the theory of quantum diffusion,<sup>7,8</sup> the exponent can take on the values 8 and 10.

The result (2.8) can be derived on the basis of the following simple arguments. The effective radius over which the relaxation occurs,  $r_*$ , is determined by equating the diffusion and relaxation times:

$$r^2/D(r) \sim 1/W(r), \text{ i.e. } r \sim a(W(a)a^2/D(a))^{1/(n+4)}.$$

On the other hand, we have  $T_{ca}^{-1} \sim 4\pi(r_*/a)^3 W(r_*)$ ; substituting in the value found for  $r_*$ , we then find (2.8).

It is convenient to express the relaxation time in terms of the two-particle-recombination time, under the assumption that the recombination radius is close to the interatomic distance:

$$T_{ca}^{-1} \approx T_{rec}^{-1} [4\pi x W(a) T_{rec}]^{(n+1)/(n+4)}, \quad (2.9)$$

$$T_{rec}^{-1} \approx \frac{4\pi x}{a^2} D(a). \quad (2.10)$$

The temperature dependence of  $T_{ca}$  is determined primarily by the dependence  $T_{rec}(T)$ , since under the condition  $T \ll \omega_0$  the value of  $W(a)$  does not depend on the temperature. The quantity  $T_{rec}$  is known quite well from experiments.<sup>1</sup> Accordingly, by measuring the dependence  $T_{ca}(T) \sim T_{rec}^{3/(n+4)}$ , one can in principle determine the behavior of the diffusion coefficient,  $D(r) \sim r^n$ .

If we were concerned with the time scale of an allowed electron transition,  $T_{cb}$  (or  $T_{da}$ ), we would have obtained precisely the same result as in (2.8), but with the quantity  $W^{cb} = (3/8\kappa^2) W^{ca}$ . The effective relaxation radius for allowed transitions is greater than that for the forbidden transition. The times  $T_{cb}$  and  $T_{ca}$  are thus related by

$$T_{cb} \approx (8\kappa^2/3)^{(n+1)/(n+4)} T_{ca}, \quad (2.11)$$

not by  $T_{cb} \sim \kappa^2 T_{ca}$  as they would be in the case of totally immobile or very rapidly moving particles. Independent measurements of  $T_{cb}$  and  $T_{ca}$  would also answer the question of the value of the exponent  $n$ .

The time  $T_{ca}$ , which is determined by the interaction of hydrogen atoms with each other, increases with decreasing concentration, and at small values of  $x$  the relaxation due to the interaction of the magnetic moment of the atom with the magnetic moment of a nucleus of the orthomolecule may be important. In this case, at an orthomolecular concentration  $x_0 \sim 1$ , the relaxation time would be completely independent of the diffusion. Going through calculations similar to those involved in the derivation of (2.2) (the only change is in the matrix element of  $\hat{V}_d$  in terms of the spin variables), we find the following expression for the relaxation probability when the atom is separated from the orthomolecule by a distance  $r$ :

$$W_0(r) \approx {}^3/{}_s(\mu_p/\mu_B)^2 W(r), \quad (2.12)$$

where  $\mu_p$  is the magnetic moment of the proton.

According to the relaxation mechanism under consideration here, the time  $T_{ca}$  for a matrix with a normal concentration of orthomolecules is

$$T_{ca} \approx [{}^3/{}_i z W_0(a)]^{-1},$$

where  $z$  is the number of hydrogen molecules nearest to the atom. Comparing this result with (2.8) and (2.9), we find an estimate of that atomic hydrogen concentration  $x^*$  below which the dominant relaxation mechanism is the relaxation

of the electron spin due to the interaction with orthomolecules:

$$x^* \sim \left(\frac{\mu_p}{\mu_B}\right)^2 \left[\frac{a^2 W(a)}{2D(a)}\right]^{3/(n+4)}. \quad (2.13)$$

From experiments on the recombination of atomic hydrogen<sup>1</sup> we find the estimate  $a^2/D(a) \sim 10\text{--}100$  s of the time scale for the hop of a particle from one cell to another in neighboring coordination spheres. Taking  $n = 8$ , we find the following estimates on the basis of (2.8) with (2.2) and also (2.12) and (2.13) for the case of the H atom as an interstitial impurity in fields  $H \sim 5\text{--}10$  T:

$$T_{ca} \sim \begin{cases} 10^3 \text{ s}, & x < x^* \\ 10^{-1}/x \text{ s}, & x > x^*, \quad x^* \sim 10^{-4}. \end{cases} \quad (2.14)$$

The value found for  $T_{ca}$  agrees with experimental data.<sup>11</sup> If we assume that the H atom is a substitutional impurity, we find that the time  $T_{ca}$  is significantly greater than the experimental time, but the estimate of the concentration  $x^*$  remains essentially the same.

In principle, an exchange interaction of atoms could also cause a  $ca$  transition. However, this interaction could be important only for the very nearest coordination spheres because of the very rapid exponential decay with increasing distance between atoms. Again in this case, estimates yield  $T_{ca}^{ex} \sim 10^{-1}/xs$ . In the case of the allowed transitions  $cb$  and  $da$ , on the other hand, the role of the exchange interaction is weakened by a factor proportional to the parameter  $\kappa^2$  and can be ignored.

### 3. PHONONLESS RELAXATION OF ATOMIC HYDROGEN IN A MATRIX OF PARA-H<sub>2</sub>

Recent experiments on the relaxation of the electron spin of the H atom in an H<sub>2</sub> matrix ( $T \sim 1$  K) with a small admixture of orthomolecules in fields  $H \sim 0.1\text{--}1$  T (Ref. 10) revealed a phononless relaxation mechanism. Evidence for this conclusion comes from the fact that the time  $T_1$  is several orders of magnitude shorter than the time dictated by one-phonon process (2.2) and has the opposite dependence on the magnetic field  $T_1 \sim \omega_0^2$ .

In the case at hand we have  $\Delta < \omega_0$ , and the only possibility for phononless relaxation would arise if there were level shifts  $\xi \approx \omega_0$  in the medium. In this case the spin relaxation could occur directly upon the transition of an atom to a neighboring cell, and the change in its energy as a result of such a transition would be offset by the Zeeman energy  $\omega_0$  associated with the spin flip. In an H<sub>2</sub> crystal, such shifts would arise from the anisotropic interaction of the hydrogen atom with the orthomolecule, which would lead to a splitting of the rotational states of the orthomolecule with different angular-momentum projections. According to calculations in the literature,<sup>12,13</sup> at the interatomic distance this interaction is on the order of 1 K and falls off sharply with increasing distance between the atom and the orthomolecule. Shifts of this sort could also arise from a H-(ortho-H<sub>2</sub>) deformation interaction, but this interaction is comparatively weak. The number of different shifts for transitions of the H atom in the first two coordination spheres is quite high, on the order of  $z^2$ . This estimate is obvious when we note that not all the positions of an atom are equivalent. When the high symmetry of the lattice is taken into account, we see

that some of the states of atom near the orthomolecule have the same energy, but the coherent quantum tunneling between these states lifts the degeneracy. The characteristic distance between nearest values of the level shift,  $\Delta E$ , is on the order of the tunneling amplitude  $\Delta_0$  ( $\Delta \approx z\Delta_0$ ), which is  $\sim 10^{-2}$  K according to estimates given below. The uncontrollable broadening of each level due to the interaction with other lattice defects (impurities, vacancies, and dislocations) would apparently exceed  $\Delta E$ . There would accordingly be a quasicontinuous band of possible values of the level shift, with a width  $\Gamma \sim 1$  K. Another argument in favor of the formation of a quasicontinuous band of this sort is the presence of the band motion of the H atom beginning no later than the second or third coordination sphere ( $\Delta \sim 0.1$  K; more on this below).

Let us consider a phononless transition of the H atom from a state with an energy  $E_1$  to a state with  $E_2$  [in particular, in the two-well problem we would have  $E_{1,2} = \pm 1/2(\xi^2 + \Delta_0^2)^{1/2}$ , where  $\xi$  and  $\Delta_0/2$  are respectively the level shift and the amplitude of the tunneling between wells] accompanied by a simultaneous spin flip due to dipole spin interaction (2.1) with the nearest orthomolecule. We denote by  $A$  the amplitude for such a transition. The spin relaxation process is characterized by, in addition to the amplitude  $A$ , the lifetime  $\tau$  of an atom with a given spin projection in a certain energy level, which is determined either by the motion of the electron through the crystal or by a spin diffusion process. We assume that the temperature of the system satisfies  $T \gtrsim \omega_0$ . For the relaxation time we can write a general expression which holds within a numerical factor over the entire ranges of these parameters:

$$T_1^{-1} \sim \frac{1}{N} \sum_{E_1, E_2} \frac{1}{\tau} \frac{A^2}{(A, 1/\tau)_{\max}^2 + (E_1 - E_2 - \omega_0)^2}, \quad (3.1)$$

where  $N$  is the number of unit cells. By virtue of the condition  $T \gtrsim \omega_0$  we can omit the Gibbs factor, which reflects the occupation numbers of  $E_1$  and  $E_2$ , from (3.1), and we can assume that the time  $\tau$  is the same for atoms with different spin projections. The summation over  $E_1$  and  $E_2$  in (3.1) corresponds to independent contributions to the relaxation from different transitions in the system formed by an atom near an orthomolecule. The presence of a quasicontinuous band of values of the level shift means that we can replace the summation in (3.1) by an integration:

$$\sum_{E_1, E_2} \rightarrow Nx_0 z^2 \int \frac{d(E_1 - E_2)}{\Gamma}$$

( $x_0$  is the concentration of orthomolecules). We then find

$$T_1^{-1} \sim \frac{x_0 z^2}{\tau} \frac{A^2}{(A, 1/\tau)_{\max} \Gamma}. \quad (3.2)$$

The transition amplitude  $A$  is given by

$$A_{12}^{\sigma\sigma'} = \langle \sigma E_1 | \hat{V}_d(\mathbf{r}) | \sigma' E_2 \rangle, \quad (3.3)$$

where  $r$  is the distance from the atom to the center of mass of the orthomolecule, and  $\sigma$  and  $\sigma'$  are the spin states of the atom-orthomolecule system. Evaluating the matrix element (3.3) for the two-well situation, we find

$$A_{12}^{\sigma\sigma'} \approx \left\langle \sigma \left| \frac{\partial \hat{V}_d'(\mathbf{r})}{\partial \mathbf{r}} \right| \sigma' \right\rangle g \frac{\Delta_0}{E_1 - E_2} \Big|_{E_1 - E_2 \approx \omega_0}, \quad (3.4)$$

where  $\mathbf{g}$  is the distance between wells. Since the angular dependence of expression (3.4) is rather complicated, it is more convenient to consider the quantity  $A^2 = \langle |A_{12}^{\sigma\sigma'}|^2 \rangle$ , where  $\langle \dots \rangle$  means an average over the angles of the vectors  $\mathbf{r}$  and  $\mathbf{g}$  and also the trace over the spin variables of the orthomolecule. Direct calculations yield

$$A^2 = \frac{40}{3} \left( \frac{\mu_B \mu_P}{r^3} \right)^2 \left( \frac{\Delta_0}{\omega_0} \right)^2 \left( \frac{a}{r} \right)^2. \quad (3.5)$$

It follows from (3.2) that under the condition  $1/\tau \ll A$  the relaxation is diffusion-controlled, while in the opposite limit it is totally independent of  $\tau$ . It is this case which corresponds to the dependence  $T_1 \sim H^2$  found experimentally. Using expression (3.5) for the transition amplitude, we find ( $r \sim a$ )

$$T_1^{-1} \sim 10z^2 x_0 \frac{\Delta_0^2}{\Gamma} \left( \frac{\mu_B \mu_P}{a^3 \omega_0} \right)^2. \quad (3.6)$$

Taking the experimental value of  $T_1$  for various concentrations of the orthomolecule,<sup>10</sup>  $x_0$ , we find  $\Delta_0 \sim 10^{-2}$  from (3.6). This value corresponds to a width  $\Delta \sim 10^{-1}$  K of the coherent-motion band. This result agrees with the estimate of  $\Delta$  from data on the recombination of H atoms.

The condition  $1/\tau \gg A$  imposes an upper limit on the lifetime of an atom with a given spin projection in a cell:  $\tau \lesssim 10^{-5}$  s. The reason for the order of magnitude of  $\tau$  may be, in particular, the spin diffusion resulting from an interaction with other hydrogen atoms, if their concentration satisfies  $x \gtrsim 10^{-5}$ .

If the atomic concentration is high, it is worthwhile to examine the corresponding phononless relaxation process caused by the spin dipole interaction of a hydrogen atom near an orthomolecule with an atom a fair distance away ( $1/T_1 \sim x_0 x$ ). The distance between atoms must be large because in the opposite case the existence of the strong long-range interaction with a second atom near the orthomolecule would prevent the formation of a quasicontinuous band for the values of the level shift. This circumstance and also the concentration factor  $x$  offset to a large extent the increase in the relaxation probability due to the substitution  $\mu_p \rightarrow \mu_B$ .

In principle, this relaxation mechanism could operate when two H atoms far from an orthomolecule come close together and there is a random coincidence of a level shift with the value of  $\omega_0$ . In this case, however, the dependence of  $T_1^{-1}$  on the magnetic field should have a sharp peak, in contradiction of the experimental data of Ref. 10.

#### 4. BLOEMBERGEN RELAXATION MECHANISM FOR HE<sup>3</sup> ATOMS IN THE HE<sup>4</sup> CRYSTAL

For impurity He<sup>3</sup> atoms in the He<sup>4</sup> crystal in a weak magnetic field ( $H \lesssim 0.1$  T) the Zeeman transition energy is  $\omega_0 \ll \Delta$  ( $\Delta \sim 10^{-4}$  K; Refs. 3-5), and the Bloembergen phononless relaxation mechanism should operate, with conversion of the energy  $\omega_0$  into the energy of band motion. In this case, however, the Bloembergen mechanism has an unusual feature, which stems from the existence of regions of slow, diffusive particle motion ( $\xi \gg \Delta_0$ ) in addition to the region of band motion ( $\xi < \Delta_0$ ). The typical value of the level shifts which arise when two He<sup>3</sup> particles come close together is  $\sim 10^{-2}$  K in the first coordination sphere. If the temperature is sufficiently low, spin relaxation in the case of a slow clos-

ing ( $\Delta/\xi \sim 10^{-2}$ ) of the particles outside the region of the band motion would be ineffective. However, the states of a pair of particles separated by the interatomic distance would be energy-degenerate in the basal planes of the lattice by virtue of the symmetry of the crystal. This circumstance would give rise to the formation of a band for the two-dimensional motion of such a pair.<sup>5,14-16</sup> The typical correlation time here, as in the case of ordinary band motion, would be  $\tau \sim 1/\Delta$ , and the inverse longitudinal relaxation time

$$T_1^{-1} \sim zxV_d^2(a)/\Delta \quad (4.1)$$

would be independent of the temperature.<sup>5,14,15</sup>

Relation (4.1), which is familiar, corresponds to the regime of "weak" collisions, in which the probability for relaxation in a pair,  $V_d^2(a)/\Delta$  is small in comparison with the probability for the formation and decay of the pair,  $1/\tau_D$ . The value of  $1/\tau_D$  is related to the diffusion of particles in the case of pronounced shifts by a vacancy or two-phonon mechanism. In practice, the parameter values of the system are such that the conditions under which the collisions can be considered "weak" hold over the entire temperature interval  $T > 0.5$  K which has been studied experimentally to date.<sup>17</sup> As the temperature is reduced, however, the diffusion decreases sharply, and it becomes the process which primarily determines the longitudinal relaxation at  $T < T^*$ , where

$$1/\tau_D(T^*) \approx V_d^2(a)/\Delta. \quad (4.2)$$

From this point on, the time  $T_1$  satisfies

$$T_1^{-1} \sim zx/\tau_D(T), \quad (4.3)$$

and it increases sharply with decreasing temperature. The increase is approximately exponential, since direct estimates based on the experimental data show that  $\tau_D(T^*)$  in the nearest coordination spheres, with  $\xi \gg \Delta$ , is determined by a vacancy diffusion mechanism. For a vacancy activation energy  $T_a \sim 10$  K these estimates yield

$$T^* \approx (0.5-0.4) \text{ K}. \quad (4.4)$$

As the temperature is reduced further from  $T^*$ , the functional dependence  $T_1(T)$  may become a step function because of the possibility of band motion of a pair formed at two or more interatomic distances (Fig. 1). With increasing distance between the impurity particles, however, there is a sharp increase in the number of types of bound pairs, for each of which there are many branches in the energy spec-

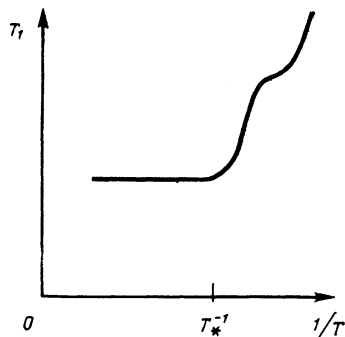


FIG. 1. Temperature dependence of the longitudinal relaxation time.

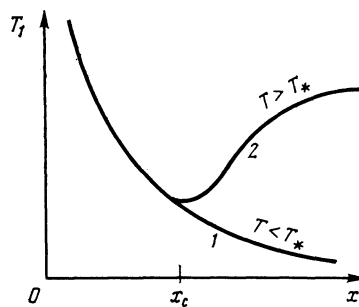


FIG. 2. Concentration dependence of the longitudinal relaxation time.

trum.<sup>18</sup> A step function should thus be smoothed over quite rapidly (in practice, one could apparently observe one or two steps).

If the concentration of He<sup>3</sup> atoms is sufficiently high,  $x > x_c$ , and the level shift at the average distance between atoms satisfies

$$\xi(\bar{R})|_{x=x_c} \gg \Delta, \quad (4.5)$$

a static disruption of the band comes into play. The scale value of the level shift at the average distance  $\bar{R}$  given by (2.3) is, in the case of a deformation interaction,

$$\xi(\bar{R}) \sim \xi(a) \left(\frac{a}{\bar{R}}\right)^4 \sim \Delta \frac{\xi(a)}{\Delta} (x)^{1/3} \equiv \Delta \left(\frac{x}{x_c}\right)^{1/3}. \quad (4.6)$$

Using  $\xi(a)/\Delta \sim 10^2$ , we find the estimate  $x_c \gtrsim 10^{-2}$ . In the situation under consideration here, the values of the level shift form a continuous band with a width on the order of  $\xi(\bar{R})$ , and we can use the result (3.2) for  $T_1$ . Noting that the condition  $\omega_0 \ll \Delta$  means that the amplitude which figures in (3.2) satisfies  $A \sim V_d(a)$  and that the characteristic correlation time at a site for shifts  $\xi \sim \Delta_0$  is  $1/\tau \sim \Delta \gg V_d(a)$ , we find

$$T_1^{-1} \sim zxV_d^2(a) \xi^{-1}(\bar{R}). \quad (4.7)$$

The quantity  $T_1$  determined by (4.7) determines the relaxation time of pairs of atoms in the weak-collision regime. In this case the longitudinal relaxation time has an anomalous concentration dependence:  $T_1 \sim x^{1/3}$  (line 2 in Fig. 2).

The characteristic temperature  $T^*$ , below which the longitudinal relaxation becomes diffusion-controlled, is now found from the relation [cf. (4.2)]

$$\tau_D^{-1}(T^*) \sim V_d^2(a)/\xi(\bar{R}). \quad (4.8)$$

Expression (4.3) remains in force for the relaxation rate.

The temperature dependence of the transverse relaxation time  $T_2$  is characterized by a diffusive narrowing of the line at high  $T$  and by a plateau which corresponds to a rigid lattice,

$$T_2^{-1} \sim V_d(\bar{R}) \sim \pi x V_d(a), \quad (4.9)$$

at temperatures for which the motion becomes quite slow, and the relation  $V_d(a)\tau_D \gg 1$  (see Ref. 17 and Fig. 3 of the present paper).

If the interaction between particles were diffusive throughout the volume,  $T_2$  would remain at the plateau level down to  $T = 0$ . Such a situation clearly holds in the case  $x > x_c$ , in which the band motion is suppressed over the entire volume of the crystal.

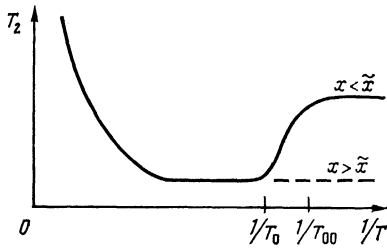


FIG. 3. Transverse relaxation time as a function of the temperature and the concentration of He<sup>3</sup> atoms.

At  $x < x_c$ , the existence of the band motion at large distances between particles may change the picture fundamentally. Curvature of the band in the strain interaction potential  $U(r)$  of the He<sup>3</sup> atoms would have the consequence that within the framework of the band motion the particles could approach each other only to a distance on the order of  $R_0$ , where

$$U(R_0) \approx \Delta. \quad (4.10)$$

In the region  $r > R_0$ , the transverse relaxation is substantially lower than (4.9) because of the dynamic contraction. A critical role is thus played by the transition from the region of the band motion into the diffusive region of slow motion,  $r, R_0$ , which is inelastic. This transition might occur by two mechanisms. If the impurity concentration is sufficiently low, the predominant mechanism would be two-phonon scattering, from which we find the transition probability

$$W_{ph} = \frac{4\pi R_0^2 x D_{ph}(R_0)}{a^4} \approx \frac{4\pi R_0^2}{a^2} x \Omega_{ph} \sim T^0, \quad (4.11)$$

where  $D_{ph} \sim a^2 10^6 \Theta_D (T/\Theta_D)^9$  is the two-phonon diffusion coefficient for level shifts  $\xi \lesssim \Delta_0$  ( $\Theta_D$  is the Debye temperature). At temperatures below the temperature  $T_0$  defined by

$$V_d(a) a^2 / 4R_0^2 \sim \Omega_{ph}(T_0), \quad (4.12)$$

the transition probability  $W_{ph}$  given by (4.12) becomes smaller than relaxation probability (4.9). In this case we find the relation  $T_2^{-1} \approx W_{ph}$ , and the time  $T_2$  begins to increase sharply with decreasing  $T$ .

Because of the sharp decrease in  $W_{ph}(T)$  with decreasing temperature, the other mechanism for an inelastic transition from the region of band motion into the diffusive region, involving interaction with a third particle, rapidly becomes dominant. When one of the particles of a pair of interest (particles 1 and 2) interacts with a third particle, an energy on the order of  $\Delta \sim z\Delta_0$  can be transferred to it. The cross section for inelastic scattering of this sort of particle 1 (or 2) with a third particle satisfies  $\sim a^2$ . Taking this result into account, we find the following expression for the transition probability:

$$W_{im} \approx 4\pi (R_0/a)^2 x \Omega_{im}, \quad \Omega_{im} \sim \Delta_0 x. \quad (4.13)$$

At temperatures  $T < T_{00}$  where  $T_{00}$  is determined by the condition  $\Omega_{ph}(T_{00}) = \Omega_{im}$ , the transverse relaxation is determined by the probability  $W_{im}$ . Correspondingly, we have a time  $T_2 \sim 1/x^2$ , which becomes independent of the temperature.

The value of the critical concentration  $\tilde{x}$ , at which the

relaxation probability given by (4.9) becomes the same at  $W_{im}$  as given by (4.13), is

$$\tilde{x} \approx \frac{V_d(a)}{\Delta_0} \left( \frac{a}{R_0} \right)^2. \quad (4.14)$$

This condition of course agrees with the condition  $T_0 = T_{00}$ . For  $x > \tilde{x}$ , the value of  $T_2$  at the minimum level, (4.9), persists down to temperature  $T = 0$  (Fig. 3).

This behavior of  $T_2$  as a function of the temperature and the concentration agrees qualitatively with the experimental observations of Refs. 17 and 19. The known values of the parameters of the theory (Ref. 8, for example) lead to estimates  $T_0 \approx 0.7-0.6$  K and  $\tilde{x} \approx 10^{-3} \ll x_c$ , in agreement with experimental data.

Note that for transverse relaxation under the condition  $x < x_c$  the approach of the particles simply to a distance  $a \ll R < R_0$  is important—not the formation of an He<sup>3</sup> quasimolecule at the interatomic distance (as was suggested in Ref. 19). Furthermore, in this situation the formation of a quasimolecule of this sort due to an interaction between impurity particles would be essentially impossible ( $\xi \gg \Delta$ ).

Bloembergen's approach to determining the relaxation times  $T_1$  and  $T_2$ , which is the one customarily taken and the approach which we have taken in this section of the paper, is only approximate since it is based on a phenomenological exponential correlation function. Many modifications of this approach have been proposed; they make it possible to find this function in the regime of "weak" collisions for the case of a coordinate-independent diffusion coefficient or a band motion. In principle, there is a general approach to this problem which would make it possible to determine the times  $T_1$  and  $T_2$  from a kinetic equation, and for an arbitrary functional dependence  $D(r)$ . That equation is derived in the Appendix to the present paper.

We are indebted to Yu. M. Kagan for interest in this study and for useful discussions.

## APPENDIX

We introduce the two-particle distribution function  $f(\mathbf{r})$ , which is the probability for finding two particles separated by a distance  $\mathbf{r}$  (for noninteracting particles we would have  $f = x^2 = \text{const}$ ). This function is determined by an equation of the form

$$\partial f / \partial t + \hat{L}(f) = 0, \quad \hat{L}(f) = -\text{div } 2D \nabla f. \quad (A1)$$

Since the spin dipole interaction is weak [ $V_d(a) \ll \xi, \Delta$ ], it cannot influence the diffusion of the particles, and we are justified in treating the relaxation of the spin of the particles against the background of a given motion of the particles. At a formal level, this circumstance can be incorporated quite easily by treating  $f(\mathbf{r})$  as a density matrix in the spin variables and by introducing an additional interaction term in (A1):

$$\dot{f} + \hat{L}(f) + i[\hat{V}_d, f] = 0. \quad (A2)$$

We rewrite Eq. (A2) in integrodifferential form:

$$\dot{f} + \hat{L}(f) = -i[V_d(\mathbf{r}, t), f_0] - \int_0^t d\tau \int d\mathbf{r}' G(\mathbf{r}, \mathbf{r}', \tau) \times [\hat{V}_d(\mathbf{r}, t), [\hat{V}_d(\mathbf{r}', t - \tau), \hat{f}(\mathbf{r}', t - \tau)]], \quad (A3)$$

where  $G$  is the Green's function of Eq. (A1), and  $\hat{f}_0 = \hat{f}(\mathbf{r}, 0) = \text{const}$ .

The Green's function  $G(\mathbf{r}, \mathbf{r}', t)$  on the right side of Eq. (A1), which determines the spatial correlations in the arrangement of a given pair of particles, changes substantially over diffusion times  $\tau_D$ . Since the concentration of impurity atoms is small, the relaxation of the average spin of the system occurs over times  $t \gg \tau_D$ , when a large fraction of the atoms undergoes collisions. We can thus replace the temporal argument of  $\hat{f}(\mathbf{r}', t - \tau)$  on the right side of (A3) by  $t$ , and we can replace the upper limit on the integration over  $\tau$  by infinity. Since the integral over  $d\mathbf{r}'$  is taken near the point  $\mathbf{r}' = \mathbf{r}$  [as can be seen by substituting the expressions for  $V_d$  and  $G$  into (A3)], we also replace the spatial coordinate  $\mathbf{r}'$  in  $\hat{f}(\mathbf{r}', t)$  by  $\mathbf{r}$ . As a result we find a differential equation for the distribution function. We are actually interested not in  $\hat{f}(\mathbf{r})$  but in the integral quantity  $\int \hat{f}(\mathbf{r}) d\mathbf{r}$ , which is proportional to the average spin of the system. We accordingly integrate Eq. (A3) over the angular variables. For the function

$$\hat{f}(\mathbf{r}) = \int \frac{d\mathbf{n}}{4\pi} \hat{f}(\mathbf{x})$$

we then find the equation (we are dealing with spin-1/2 particles)

$$\dot{\hat{f}}(\mathbf{r}, t) = \frac{2}{r^2} \frac{\partial}{\partial r} r^2 D(r) \frac{\partial}{\partial r} \hat{f}(\mathbf{r}, t) - \frac{\mu^4}{r^3} \sum_q \int \frac{d\tau d\mathbf{r}'}{r'} \times [S^q, [S^q, \hat{f}(\mathbf{r}, t)]] e^{iq\omega_0 \tau} G_2(\mathbf{r}, \mathbf{r}', t), \quad (\text{A4})$$

where

$$G_2(\mathbf{r}, \mathbf{r}', t) = \int \frac{d\mathbf{n}_{rr'}}{4\pi} P_2(\mathbf{n}, \mathbf{n}') G(\mathbf{r}, \mathbf{r}', t),$$

and  $P_2(\mathbf{n}, \mathbf{n}')$  is the Legendre polynomial.

To determine the time evolution of the average spin of the two particles,  $\mathbf{S}$ , we multiply both sides of (A4) by the operator  $(\mathbf{S}_1 + \mathbf{S}_2)$ , and take the trace. Taking the trace by the standard procedure (Ref. 6, for example), we find

$$\begin{aligned} \frac{\partial S_\alpha}{\partial t} &= \frac{2}{r^2} \frac{\partial}{\partial r} r^2 D(r) \frac{\partial}{\partial r} S_\alpha \\ &\quad - \frac{9}{20} \frac{\mu^4}{r^3} \left\{ 4\pi \int_0^\infty \frac{d\mathbf{r}'}{r'} d\tau G_2(\mathbf{r}, \mathbf{r}', \tau) F_\alpha(\tau) \right\} S_\alpha, \\ \alpha &= (x, y, z), \\ F_x = F_y &= 1 + \frac{5}{3} \cos \omega_0 t + \frac{2}{3} \cos 2\omega_0 t, \\ F_z &= \frac{2}{3} \cos \omega_0 t + \frac{8}{3} \cos 2\omega_0 t. \end{aligned} \quad (\text{A5})$$

From the differential equation (A5) in the quasisteady approximation ( $x \ll 1$ ) we can find the quantities  $(\partial S_x / \partial r)|_{r \rightarrow \infty}$  and  $(\partial S_x / \partial r)|_{r \rightarrow \infty}$ , which determine the longitudinal and transverse relaxation times.

The second term on the right side of (A5) describes the relaxation of the spin of a pair of particles in a collision. If the diffusion is very fast, and  $G_2$  varies over times  $\tau_D \ll 1/\omega_0$ , we have  $F_x \approx F_z \approx 10/3$ . In the opposite limit  $\tau_D \gg 1/\omega_0$ , it is sufficient to retain in  $F_x$  only the time-independent part:

$F_x = 1$ . In each of these limiting cases, the relaxation term in (A5) takes a particularly simple form: The integration over  $d\mathbf{r} d\mathbf{r}'$  can be carried out exactly for an arbitrary power law  $D(r)$  in (2.7). In particular, with  $F_x = 1$  we find

$$\frac{\partial S_x}{\partial t} = \frac{2}{r^2} \frac{\partial}{\partial r} r^2 D(r) \frac{\partial}{\partial r} S_x - \frac{3}{80} \frac{\mu^4}{r^4 D(r)} S_x. \quad (\text{A6})$$

From the solution of this equation we find the following expression for the reciprocal of the transverse relaxation time:

$$\begin{aligned} T_2^{-1} &= \frac{4\pi r^2 D(r)}{x} \frac{\partial S_x}{\partial r} \Big|_{r \rightarrow \infty} \\ &= 4\pi \left( \frac{3}{40} \right)^{1/2} x \omega_a \text{th} \left[ \frac{\omega_a a^2}{D(a)} \left( \frac{3A}{40} \right)^{1/2} \right], \end{aligned} \quad (\text{A7})$$

where

$$A = aD(a) \int_a^\infty \frac{dr}{r^2 D(r)}, \quad \omega_a = \frac{\mu^4}{a^3}.$$

In the limit of "weak" collisions,  $\tau_D^{-1} \sim D(a)/a^2 \gg \omega_a$ , expression (A7) agrees to within a numerical factor with Bloembergen's formula, with a correlation time  $\tau = a^2/D(a)$ . In the opposite limit, (A7) yields the result corresponding to a rigid lattice:

$$T_2^{-1} = \left( \frac{8}{3} \right)^{1/2} \pi x \omega_a. \quad (\text{A8})$$

<sup>1</sup>A. Ya. Katunin, I. I. Lukashvits, S. T. Orozmatov, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **34**, 375 (1981) [JETP Lett. **34**, 357 (1981)].

<sup>2</sup>A. Ya. Katunin, I. I. Lukashvits, V. V. Sklyareskiĭ, *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 391 (1982) [JETP Lett. **36**, 472 (1982)].

<sup>3</sup>R. A. Guyer, R. C. Richardson, and L. I. Zane, Rev. Mod. Phys. **43**, 532 (1971).

<sup>4</sup>V. N. Grigor'ev, B. N. Esel'son, and V. A. Mikheev, Fiz. Nizk. Temp. **1**, 5 (1975) [Sov. J. Low Temp. Phys. **1**, 1 (1975)].

<sup>5</sup>M. G. Richards, J. H. Smith, P. S. Tofts, and W. J. Mullin, Phys. Rev. Lett. **34**, 1545 (1975).

<sup>6</sup>A. Abragam, *The Principles of Nuclear Magnetism*, Oxford Univ. Press, London, 1961.

<sup>7</sup>Yu. Kagan, L. A. Maksimov, and N. V. Prokof'ev, Pis'ma Zh. Eksp. Teor. Fiz. **36**, 204 (1982) [JETP Lett. **36**, 253 (1982)].

<sup>8</sup>Yu. Kagan and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **84**, 792 (1983) [Sov. Phys. JETP **57**, 459 (1983)].

<sup>9</sup>Yu. M. Kagan, in: Defects in Insulating Crystals. Proceedings of an International Conference, Riga, May 1961, Springer-Verlag, New York.

<sup>10</sup>A. S. Iskovskikh, A. Ya. Katunin, I. I. Lukashvits, *et al.*, Zh. Eksp. Teor. Fiz. **91**, 1085 (1986) [Sov. Phys. JETP **64**, 1832 (1986)].

<sup>11</sup>A. Ya. Katunin, I. I. Lukashvich, S. T. Orozmatov, *et al.*, Phys. Lett. **87A**, 483 (1982).

<sup>12</sup>A. Dalgarno, R. J. W. Henry, and C. S. Roberts, Proc. Phys. Soc. **88**, 611 (1966).

<sup>13</sup>P. Sieghban and B. Lui, J. Chem. Phys. **68**, 2457 (1978); D. G. Truhlar and C. J. Horowitz, J. Chem. Phys. **68**, 2466 (1978).

<sup>14</sup>J. E. Sacco and A. J. Widom, Low Temp. Phys. **24**, 241 (1975).

<sup>15</sup>W. J. Mullin, R. A. Guyer, and H. A. Goldberg, Phys. Rev. Lett. **35**, 1007 (1975).

<sup>16</sup>A. F. Andreev, Zh. Eksp. Teor. Fiz. **68**, 2341 (1975) [Sov. Phys. JETP **41**, 1170 (1975)].

<sup>17</sup>A. R. Allen, M. G. Richards, and J. Schratte, J. Low Temp. Phys. **47**, 289 (1982).

<sup>18</sup>A. É Meĭerovits, Zh. Eksp. Teor. Fiz. **69**, 1325 (1975) [Sov. Phys. JETP **42**, 676 (1975)].

<sup>19</sup>J. Schratte, A. R. Allen, and M. G. Richards, J. Low Temp. Phys. **57**, 179 (1984).

Translated by Dave Parsons