[6]A. B. Roĭtsin, Fiz. Tverd. Tela (Leningrad) 5, 2395 (1963) [Sov. Phys. Solid State 5, 1743 (1964)].
[7]J. H. Mackey, J. W. Boss, and D. E. Wood, J. Magn. Res. 3, 44 (1970).
[8]R. Schnadt and H. Schneider, Phys. Kondens. Mater, 11, 19 (1970).
[9]A. L. Taylor and C. W. Farnell, Can. J. Phys. 42, 595 (1964). A. B. Brik, I. V. Matyash, S. M. Litovchenko, and M. I. Samoĭlovich, Fiz. Tverd. Tela (Leningrad) 22, 3161 (1980) [Sov. Phys. Solid State 22, 1849 (1980)].
[10]A. B. Roitsin, Usp. Fiz. Nauk 105, 677 (1971) [Sov. Phys. Usp.
[11]W. J. De Vos and J. Volger, Physica 47, 13 (1970).
[12]I. N. Geĭfman, M. D. Glinchuk, M. F. Deĭgen, and B. N. Krulinkovskiĭ, Zh. Eksp. Teor. Fiz. 74, 164 (1978) [Sov. Phys. JETP 47, 84 (1978)].

Translated by J. G. Adashko

Effect of vacancies on NMR is solid He^3

I. N. Piradashvili

Physics Institute, Georgian Academy of Sciences
(Submitted 5 May 1980)
Zh. Eksp. Teor. Fiz. 79, 1908–1920 (November 1980)

The influence of ferromagnetically polarized regions (FPR) produced by vacancies in solid He$_3$ on the spin-lattice and spin-spin relaxation times and on the spin diffusion coefficient is investigated. The FPR absorption line shape is calculated for nonequilibrium vacancy densities at $T \sim 10^{-2}$ K. The values of the FPR diffusion coefficient of the numbers of the spins contained in the FPR are determined from an analysis of the experimental data.

PACS numbers: 67.80.Mg

1. INTRODUCTION

The principal characteristic feature of a quantum crystal is the large amplitude of the zero-point vibrations of its atoms and their delocalization as a result of the overlap of the atomic wave functions. The quantum-mechanical tunneling ability manifests itself in the existence of an excitation system that is absent from non-quantum crystals. The mobility of these quasiparticles and their interaction is easy to investigate in solid He^3, since the presence of spin-$\frac{1}{2}$ particles in it permits the use of the sensitive methods of nuclear magnetic resonance (NMR).

The available experimental data on NMR in solid He^3 are summarized mainly in the review of Guver *et al.*[1] The system of nuclear spins (Z) in a constant external magnetic field H_0, described by a Zeeman Hamiltonian, arrives at thermal equilibrium with a definite temperature (spin-spin relaxation) via a dipole-dipole interaction that is modulated by the motion by one of the types of the quasiparticles. The same mechanism is responsible also for the spin-lattice relaxation.

The first part of the paper deals with the temperature region $T \sim 1.5$ K, where the dipole-dipole interaction is modulated by delocalized vacancies—vacancions (V).

In Ref. 1, the vacancion is regarded as a "bare" quasiparticle that moves through a homogeneous medium. Yet a vecancion in solid He^3 produces around itself a ferromagnetically polarized region (FPR) of nuclear spins,[2] and this region influences substantially the vacancion mobility.[3] The character of the modulation of the dipole-dipole interaction is thereby altered.

We derive below the dependences of the spin-lattice and spin-spin relaxation times, as well as of the diffusion coefficient D_Z of the nuclear magnetization, on the size and mobility of the FPR. Reduction of the experimental data[4-6] by means of these formulas makes it possible to determine the number of spins contained in the FPR and the diffusion coefficient D_V of a vacancion "dressed" in this manner, and to estimate its band width.

At $T < 10^{-2}$ K the FPR can be regarded as almost immobile,[3] so that their influence on a nonstationary process such as relaxation is very small even for large (nonequilibrium) FPR densities. On the other hand, the strong exchange interaction between the He^3 nuclei leads to a relation between the direction of the FPR magnetic moment and the polarization of the nuclear paramagnet. By the same token, the existence of the FPR influences the absorption line shape in the case of stationary detection of the NMR signal. In the second part of the paper, this dependence is derived for weak and strong constant magnetic fields.

The conclusion deals with the conditions under which the results are valid, and contains some numerical estimates.

2. RELAXATION AND DIFFUSION

Relaxation times

At $T \sim 1.5$ K the V system is closely coupled to the lattice and they have the same constant temperature. The temperature of the Z system, which is "heated" by the RF field, approaches asymptotically the temperature of the V system. The large mobility of the nuclear spins in solid He^3 leads to a rapid change of the Hamiltonian of the dipole-dipole interaction, so that it is possible to use for the calculations the short-correlation-times approximation (see Ref. 7, Chap. VIII). We ob-

0038-5646/80/110963-07$02.40

tain the correlation function that ensues from this approach and ascertain the dependence of the correlation time on the size and mobility of the FPR.

The dipole-dipole interaction in the Z system is described by the Hamiltonian $\mathscr{H}_d$:

$$\mathscr{H}_d=\sum_{q=-2}^{2}\sum_{i<j}B_{ij}^{q}S_{ij}^{q}, \tag{2.1}$$

where S_{ij}^{q} is an operator acting on the spins of the particles i and j; B_{ij}^{q} is a random function of the relative locations of the particles i and j.

Standard calculations lead to the following expression for the spin-lattice relaxation times 1:

$$T_1^{-1}=J_1(\omega_0)+4J_2(\omega_0), \tag{2.2}$$

where the spectral densities $J_q(\omega)$ of the correlation functions are in the case of polycrystalline samples

$$J_q(\omega)={}^2/_3M_2\,\mathrm{Re}\int_0^\infty g(t)e^{-iq\omega t}dt, \tag{2.3}$$

where M_2 is the Van Vleck second moment for the Hamiltonian $\mathscr{H}_d$, and $g(t)$ is the reduced correlation function of the random function $B_{ij}(t)$ and is equal, by definition to the probability of $B_{ij}(t)$ remaining constant during the time t;

$$\omega_0=-\gamma H_0 \tag{2.4}$$

is the Larmor frequency; γ is the gyromagnetic ratio.

Since the dipole-dipole interaction radius is small, it can be assumed that the change of the local magnetic field at the point $\mathbf{r}_k$ is connected with the change if its immediate spin surrounding. In the considered temperature region, the mobility and density of the FPR are large enough to assume the highest-frequency changes of the local field to be the result of passages of the FPR through the point $\mathbf{r}_k$. Let us find the probability that an immobile k-th spin located at the instant $t=0$ in a paramagnetic region "survives" a time t, i.e., does not land in any of the diffusing FPR. A spin that lands in an FPR is excluded from the "survivors," so that the sought probability is obtained by solving the equivalent problem of diffuse motion of a spin with diffusion coefficient D_V in a medium with randomly distributed immobile and absolutely absorbing spheres of radius R_0 (R_0 is the radius of the FPR and D_V is its diffusion coefficient). The corresponding aggregate of boundary conditions for the probability density $p(\mathbf{r},\mathbf{r}_k,0)=\delta(\mathbf{r}-\mathbf{r}_k)$, takes the form

$$p(\mathbf{R}_i+\mathbf{R}_0,\mathbf{r}_k,t)=0, \tag{2.5}$$

where $\mathbf{R}_i$ are the radius-vectors of the vacancies. For times

$$t>\tau\sim l^2/D_V \tag{2.6}$$

(l is the average distance between the FPR) we have a quasistationary case, and the approximate solution of the diffusion equation with the boundary condition (2.5), in the case when there is only one FPR, is of the form

$$p_i(\mathbf{r},\mathbf{r}_k,t)=(4\pi D_Vt)^{-3/2}(1-R_0/|\mathbf{r}-\mathbf{R}_i|)\exp\{-(\mathbf{r}-\mathbf{r}_k)^2/4D_Vt\}. \tag{2.7}$$

The total probability that the k-th spin will not land in a single FPR is

$$P_i(\mathbf{r}_k,t)=\int_\Omega p_i(\mathbf{r},\mathbf{r}_k,t)\,d\mathbf{r}$$

(Ω is the volume outside the FPR) and can change only as a result of "running off" into an FPR. It can therefore be determined by integrating the continuity equation

$$\dot{P}_i=\oint j_n ds \tag{2.8}$$

with initial condition $P_i(\mathbf{r}_k,0)=1$, where

$$j_n=-D_V\nabla_n p_i \tag{2.9}$$

is the normal component of the probability flux density through the FPR boundary; ds is the FPR surface element.

Changing, for simplicity, to a coordinate system with center at the point $\mathbf{r}_k$, we obtain for the considered case

$$P_i(t)=1-\frac{R_0}{|\mathbf{R}_i+\mathbf{R}_0|}\,\mathrm{erfc}\left(\frac{|\mathbf{R}_i+\mathbf{R}_0|}{2(D_Vt)^{1/2}}\right), \tag{2.10}$$

where

$$\mathrm{erfc}\,z=2\pi^{-1/2}\int_z^\infty e^{-y^2}dy$$

is the complementary probability integral.

The sought probability—the correlation function $g(t)$—is equal to

$$g(t)=\prod_i P_i. \tag{2.11}$$

Changing over in $\ln g(t)$ to the "gas" approximation

$$\sum_i\to4\pi N\int_{R_0}^\infty R^2dR,$$

where N is the vacancy density, we find that for times satisfying the condition (2.6), the correlation function is exponential

$$g(t)=\exp(-t/\tau_c) \tag{2.12}$$

and the correlation time is

$$\tau_c=(4\pi NR_0D_V)^{-1}=(4\pi x\rho R_0D_V)^{-1}, \tag{2.13}$$

where ρ is the density of the solid He^3; x is the vacancy density in the crystal. We note that $\tau/\tau_c\sim R_0/l\ll1$, and since we are considering integrals of time for which the short-correlation-time approximation is valid,

$$\Delta t\gg\tau_c, \tag{2.14}$$

the condition (2.6) is satisfied automatically. Substituting (2.12) in (2.3) we obtain for (2.2)

$$T_1^{-1}=\frac{2}{3}M_2\left[\frac{\tau_c}{1+(\omega_0\tau_c)^2}+\frac{4\tau_c}{1+4(\omega_0\tau_c)^2}\right]. \tag{2.15}$$

The vacancion mechanism considered above determines also the thermalization of the Z system (making the spin-temperature applicable to this system) are $T\sim1$ K. For the spin-spin relaxation time we have[1]

$$T_2^{-1}={}^3/_2J_0+{}^5/_2J_1+J_2, \tag{2.16}$$

where the J_q are determined by (2.3). Using formula (2.13),

$$T_2^{-1}=\frac{2}{3}M_2\left[\frac{3}{2}\tau_c+\frac{5}{2}\frac{\tau_c}{1+(\omega_0\tau_c)^2}+\frac{\tau_c}{1+4(\omega_0\tau_c)^2}\right]. \tag{2.17}$$

The distinctive character of the modulation of the local magnetic field is reflected in (2.15) and (2.17) via τ_c (2.13).

The diffusion coefficient. Comparison with experiment

The diffuse motion of the longitudinal and transverse components of the nuclear magnetization **m** are independent, so that a distinction must be made between the diffusion coefficient D_Z, which determines the transport $m_+ = m_x + im_y$, from the diffusion coefficient D_E, which determines the transport of the Zeeman energy connected with m_z and depends on the character of the coupling between the Z system and the lattice.[1,8] The coefficient D_Z calculated by us describes the magnetization transport connected with the spatial motion of the paramagnetic spins in the FPR.

The macroscopic Bloch equations with the diffusion term are of the form

$$\dot{m}_+ = -i\gamma H_0 m_+ - m_+/T_2 + D\nabla^2 m_+,$$
$$\dot{\mathcal{M}}_+ = -i\gamma H_0\mathcal{M}_+ - \mathcal{M}_+/T_2' + D_V\nabla^2\mathcal{M}_+, \tag{2.18}$$

where m is the magnetization of the paramagnet, D is the spin self-diffusion coefficient, $\mathcal{M}$ is the magnetization of the FPR ensemble, and T_2 is the time of transverse relaxation of this ensemble. Assuming that the deflecting RF pulse rotates the vectors m and $\mathcal{M}$ without changing their moduli, and recognizing that $\mu = \mathcal{N}\mu_0$, where μ and μ_0 are the magnetic moments of the FPR and of the He^3 nucleus, respectively, while $\mathcal{N}$ is the number of spins in the FPR, we obtain from the Curie law

$$\mathcal{M}_+/m_+ = \mathcal{M}/m = x\mathcal{N}^2. \tag{2.19}$$

Adding Eqs. (2.18) and substituting (2.19), we neglect the term with T_2' (see the Conclusion) and recognize that $\mathcal{M}_+ \ll m_+$ ($x\mathcal{N} \ll 1$). As a result we have for the measurable quantities

$$\dot{m}_+ = -i\gamma H_0 m_+ - m_+/T_2 + D_Z\nabla^2 m_+, \tag{2.20}$$

where

$$D_Z = D + D_V x\mathcal{N}^2. \tag{2.21}$$

The results call for a new look at the experimental data of Refs. 4–6. We note by way of introduction that the accuracy of the experiments considered by us is not high enough to reveal the temperature dependence of the pre-exponential factor in (2.13) the vacancy density has an exponential temperature dependence[6])

$$x = \exp(-E/T), \tag{2.22}$$

where E is the activation energy of the vacancies. Therefore in the reduction of the experimental data on the basis of formulas (2.15), (2.17), and (2.21) we shall assume that $\mathcal{N} = (4/3)\pi\rho R_0^3$ and D_V are independent of temperature. In these approximations, the analysis of the available experiments makes it possible to determine such basic characteristics of the FPR as $\mathcal{N}$ and D_V.

We consider now the spin-lattice relaxation time T_1 (2.15). It has a temperature minimum that corresponds to $\omega_0\tau_c \sim 1$ (observed experimentally[4,5]) in fields $\omega_0/2 = 4.8$–6.8 MHz at $T_{\min} = 1$–1.5 K. In the limiting cases of high and low temperatures we have respectively

$$T \gg T_{min}, \quad \omega_0\tau_c \ll 1,$$
$$T_1 = 3\cdot(10M_2\tau_c)^{-1} = 6\pi x\rho R_0 D_V (5M_2)^{-1}; \tag{2.23}$$
$$T \ll T_{min}, \quad \omega_0\tau_c \gg 1,$$
$$T_1 = 3\omega_0^2\tau_c(4M_2)^{-1} = 3\omega_0^2(16\pi M_2 x\rho R_0 D_V)^{-1} \tag{2.24}$$

A temperature dependence of the spin-spin relaxation time T_2 is observed at $T > 1$ K, which corresponds for the employed fields[4] ($\omega_0/2\pi \sim 3$ MHz) to the case $\omega_0\tau_c \ll 1$. From (2.17) we have [cf. (2.13)]

$$T_2 = 3\cdot(10M_2\tau_c)^{-1}. \tag{2.25}$$

For the temperature dependence of the diffusion coefficient D_Z, observed[4] in the same temperature range, we obtain from (2.21)

$$D_Z = D_V x\mathcal{N}^2. \tag{2.26}$$

From (2.23)–(2.26) we can obtain in the limit as $T \to \infty$ expressions for the temperature-independent parameters $\mathcal{N}$ and D_V. The logarithms of expressions (2.23)–(2.25) in conjunction with $\log D_Z$ of (2.26) constitute algebraic systems of equations, solution of which yields

$$\mathcal{N} = [(^3/_4\pi^2\rho^2)^{1/3}\cdot 6D_Z|_\infty(5M_2T_1|_\infty)^{-1}]^{3/5} \tag{2.27}$$

for (2.23) and (2.26),

$$\mathcal{N} = [(48\pi^2\rho^2)^{1/3}\cdot 4M_2D_Z|_\infty T_1|_\infty(3\omega_0^2)^{-1}]^{3/5} \tag{2.28}$$

for (2.24) and (2.26),

$$\mathcal{N} = [(^3/_4\pi^2\rho^2)^{1/3}\cdot 6D_Z|_\infty(5M_2T_2|_\infty)^{-1}]^{3/5} \tag{2.29}$$

for (2.25) and (2.26), and

$$D_V = D_Z|_\infty\mathcal{N}^{-2}. \tag{2.30}$$

Here $T_1|_\infty$, $T_2|_\infty$ to $T = \infty$ and $D_Z|_\infty$ are the corresponding values obtained by extrapolating to $T = \infty$ the experimental curves at $T \sim 1.5$ K,[4-6] corresponding to expressions (2.23)–(2.26). This reduction of the experimental data of Refs. 4 and 8 with the aid of Eqs. (2.27)–(2.30) yields $\mathcal{N} \approx 2$–5 and $D_V \approx 3\times(10^{-5}$–$10^{-6})$ cm^2/sec, in good agreement with the estimates of these quantities in Refs. 2 and 3 for the considered temperatures $T \sim 1$–1.5 K.

The data of Ref. 5 yield $\mathcal{N} \approx 20$–100 and $D_V \approx (10^{-6}$–$10^{-8})$ cm^2/sec. but the large scatter of the experimental points in that reference, which makes a reliable extrapolation impossible, casts doubts on these results.

We emphasize that $\mathcal{N} > 1$ for all the curves reduced by us, so that the results of Refs. 4–6 can be regarded as an experimental confirmation of the existence of FPR.

An estimate of the vacancion band width $\Delta \sim T(R_0/a)^5$ (Ref. 2) yields $\Delta \approx 8$–10 K (a is the distance between the atoms).

3. ABSORPTION LINE SHAPE

At $T \sim 10^{-2}$ K the equilibrium vacancy density in an He^3 crystal is negligibly small: $x \sim 10^{-12}$. The influence of the FPR on the absorption of the energy of the RF magnetic field will manifest itself when nonequilibrium vacancy densities are produced. We assume also that $T > I$ (I is the exchange integral). The line shape is described by the imaginary part of the magnetic susceptibility $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$.

Owing to the large vacancion exchange interaction, which couples the nuclear spins inside the FPR, we can neglect the internal structure of the region when it is acted upon by an external field of frequency up to $\omega \sim 10^9$ Hz, when the natural modes of the FPR begin to be excited.[9] It is necessary, however, to take into account the participation of the boundary spins in the diffusion outside the FPR, due to direct exchange between the He^3 nuclei (which is weaker than the vacancion exchange), since diffusion is the mechanism whereby the macroscopic magnetic moment of the FPR relaxes to equilibrium in the magnetic field. This leads to the principal boundary condition: the magnetization of the medium on the interface with the FPR is parallel to the magnetization of the FPR itself.

The considered alternating fields are weak enough to regard all the cases described below as far from saturation.

Weak constant field

We consider an He^3 crystal with an FPR, placed in constant magnetic field directed along the z axis, such that $\mu H_0 \ll T$, and a magnetic field $H_1 \ll H_0$ perpendicular to the constant field and rotating with frequency ω.

The imaginary part of the magnetic susceptibility introduced above is expressed in this case by the formula (see Ref. 7. Chap. III)

$$\chi''=-\frac{1}{4\pi H_1}\int n(\theta,\varphi)\mu^{(v)}do=-\frac{\mu}{4\pi H_1}\int n(\theta,\varphi)\sin\varphi\sin^2\theta d\varphi d\theta, \tag{3.1}$$

where $\mu^{(y)}$ is the y component of the FPR magnetic moment in the coordinate system that rotates with frequency ω; $n(\theta,\varphi)$ is the distribution, meaning the number of FPR per unit volume with angle θ between the vector of the magnetic moment of the FPR in the constant field $\mathbf{H}_0$ and a magnetic-moment precession phase shift φ relative to the rotating field $\mathbf{H}_1$.

The motion of the magnetization vector **M** of one FPR is completely defined by these two coordinates and constitutes a superposition of three motions: free precession of **M** around the direction of the effective field $\mathbf{H}_e = \mathbf{H}_0 + \mathbf{H}_1$; relaxation of **M** to an equilibrium position in the magnetic moment; and random thermal variation of the direction of **M** by rotation through small angles $\Delta o \sim 1/\mathcal{N}$. The last condition means that the kinetic equation that describes the variation of $n(\theta,\varphi)$ is a Fokker–Planck equation in spin space:

$$\dot{n}+\operatorname{div}\mathbf{J}=0, \tag{3.2}$$

where $\mathbf{J} = n\mathbf{v} + \Delta(fn)$ is the distribution-function flux density; $\mathbf{v}$ is the sum of the velocities of the precession and relaxation motions; $f(\theta,\varphi)$ is a function of the spin coordinates and must be calculated; the term with f describes the thermal motion of **M** in spin space.

In a spherical coordinate system that rotates with frequency ω[SCS(ω)], Eq. (3.2) takes the form

$$\begin{gathered}\dot{n}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left\{\sin\theta\left[n(\dot{\theta}_f+\dot{\theta}_R)+\frac{\partial}{\partial\theta}(fn)\right]\right\}\\+\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}\left[n\dot{\varphi}_f+\frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}(fn)\right]=0,\end{gathered} \tag{3.3}$$

where $\dot{\theta}_f$ and $\dot{\varphi}_f$ are the rates of precession around $\mathbf{H}_e$ in the SCS(ω); $\dot{\theta}_R$ is the relaxation rate ($\dot{\varphi}_R = 0$). To solve (3.3) we must express $\dot{\theta}_f$, $\dot{\varphi}_f$, and $\dot{\theta}_R$ in terms of the angles θ and φ. We neglect in this case the action of the alternating field on the FPR via the paramagnetic medium, the error being of the order of $\sim\omega_1\chi_0 H_0/M$ ($\omega_1 = -\gamma H_1$ and χ_0 is the static nuclear magnetic susceptibility of He^3).

To calculate $\dot{\theta}_R$, we consider the relaxation of the magnetization of the paramagnetic medium in a constant field $\mathbf{H}_0$. The change of the magnetization vector is the sum of the precession and of the diffusion motion of the nuclear spins:

$$\dot{\mathbf{m}}=\gamma[\mathbf{m}\times\mathbf{H}_0]+D\nabla^2\mathbf{m},\qquad \bar{m}=\Omega^{-1}\int m d\Omega=\text{const}. \tag{3.4}$$

The frequency of tunneling in self-diffusion, $\omega_t \sim 10^8$ Hz, is much larger than the reciprocal relaxation time of the medium with the FPR. Changing over to the SCS(ω_0) and neglecting the left-hand side of (3.4), we obtain

$$\nabla^2\mathbf{m}=0. \tag{3.5}$$

Expressed in components, the spherically symmetrical solution of (3.5) is

$$\begin{gathered}m_+(r)=r^{-1}R_0 m(R_0)\sin\theta,\\ m_z(r)=r^{-1}R_0[m(R_0)\cos\theta-\chi_0 H_0]+\chi_0 H_0,\end{gathered} \tag{3.6}$$

where $m(R_0)$ and $\theta(R_0)$, specified on the FPR surface, constitute the boundary conditions.

The FPR magnetization change due to the diffusion flux through its surface consists of rotation of a vector **M** of constant magnitude. The continuity equation expressed in terms of the components is

$$\begin{gathered}{}^4/_3\pi R_0^3\dot{M}_+ + \oint j_+^{(n)}ds=0,\\ {}^4/_3\pi R_0^3\dot{M}_z + \oint j_z^{(n)}ds=0,\end{gathered} \tag{3.7}$$

where

$$\mathbf{j}^{(n)}=-D\nabla_n\mathbf{m} \tag{3.8}$$

is the diffusion-flux density component normal to the FPR surface. From the principal boundary condition that the magnetization vectors be parallel it follows that

$$\dot{M}_+=M\dot{\theta}\cos\theta,\qquad \dot{M}_z=-M\dot{\theta}\sin\theta. \tag{3.9}$$

Substituting in (3.7) expressions (3.8) and (3.9), taking (3.6) into account, and integrating and eliminating from the two equations of (3.7) the modulus of $m(R_0)$, we obtain

$$\dot{\theta}_R=-\frac{\chi_0 H_0}{M}\frac{3D}{R_0^2}\sin\theta. \tag{3.10}$$

We note that time of relaxation from $\theta = \pi$ to $\theta = 0$ is 10^{-4} sec.

The calculation of $\dot{\theta}_f$ and $\dot{\varphi}_f$ is based on simple geometric considerations. The free precession around the direction of the effective field in the SCS(ω) constitutes motion of the vector **M** over the surface of a cone with angular frequency $\omega_e = (\Delta\omega^2 + \omega_1^2)^{1/2}$ ($\Delta\omega \equiv \omega - \omega_0$). The angles $\theta(t)$ and $\varphi(t)$ of interest to us are respectively the angle between the generator of the cone and the direction of the magnetic field, and the angle between the projections of the generator on the $\theta = \pi/2$

plane and the cone axis. The angle between the cone axis and the direction of the constant field H_0 is

$$\theta_H = \arcsin\frac{\omega_1}{(\Delta\omega^2+\omega_1^2)^{1/2}}.$$

Denoting the cone apex angle by θ_0, we get

$$\begin{gathered}\cos\theta(t) = \cos\theta_0\cos\theta_H + \sin\theta_0\sin\theta_H\cos(\omega_e t+\delta),\\ \sin\varphi(t) = \sin\theta_0\sin(\omega_e t+\delta)/\sin\theta(t),\end{gathered} \tag{3.11}$$

where δ is the initial phase of the precession. Differentiating (3.11), we can express after simple transformations the sought quantities in terms of θ and φ:

$$\dot\theta_f = \omega_1\sin\varphi, \quad \dot\varphi_f = \omega_1\operatorname{ctg}\theta\cos\varphi - \Delta\omega. \tag{3.12}$$

To determine $f(\theta,\varphi)$ we note that at equilibrium in a constant field H_0 the distribution-function flux density is zero in the laboratory frame. We have consequently in the SCS(ω)

$$\begin{gathered}J_\theta = n_0\dot\theta_R + \frac{\partial}{\partial\theta}(fn_0) = 0,\\ J_\varphi = n_0\dot\varphi_f + \frac{1}{\sin\theta}\frac{\partial}{\partial\varphi}(fn_0) = -n_0\Delta\omega,\end{gathered} \tag{3.13}$$

where

$$n_0 = \frac{N}{4\pi}\frac{\mu H_0}{T}\frac{\exp(\mu H_0 T^{-1}\cos\theta)}{\operatorname{sh}(\mu H_0 T^{-1})}$$

is the normalized equilibrium Boltzmann distribution function. From (3.13) we get, taking (3.12) and (3.10) into account,

$$f = -\frac{\chi_0 H_0}{M}\frac{T}{\mu H_0}\frac{3D}{R_0^2}.$$

We point out the relation

$$\dot\theta_R = f\frac{\mu H_0}{T}\sin\theta. \tag{3.14}$$

Putting $n = n_0 + n_1$, where n_1 is a nonequilibrium increment, and linearizing the kinetic Eq. (3.3) with respect to the perturbation ω_1, we obtain, with allowance for (3.10), (3.12), and (3.14), in the stationary case $\dot n = 0$:

$$\begin{gathered}\nabla_{\theta\varphi}^2\tilde n_1 + \frac{\mu H_0}{T}\frac{1}{\sin\theta}\left[\frac{\partial}{\partial\theta}(\sin^2\theta\,\tilde n_1) + \frac{\Delta\omega}{\eta}\frac{\partial}{\partial\varphi}\tilde n_1\right]\\ = \frac{\mu H_0}{T}\frac{\exp(\mu H_0 T^{-1}\cos\theta)}{\operatorname{sh}(\mu H_0 T^{-1})}\sin\varphi\left[\operatorname{ctg}\theta\left(\frac{1}{\sin\theta}-1\right) + \frac{\mu H_0}{T}\sin\theta\right],\end{gathered} \tag{3.15}$$

where

$$\tilde n_1 = \frac{4\pi f}{\omega_1 N}n_1, \quad \eta = \frac{\mu H_0}{T}f, \tag{3.16}$$

$\nabla_{\theta\varphi}^2$ is the angle part of the Laplacian. We seek the solution of (3.15) by perturbation theory, using the small parameter $\mu H_0/T \ll 1$. Confining ourselves to terms quadratic in $\mu H_0/T$, we obtain a sequence of equations for the approximations $\tilde n_1^{(i)}$:

$$\begin{gathered}\nabla_{\theta\varphi}^2\tilde n_1^{(0)} = \sin\varphi\operatorname{ctg}\theta(1/\sin\theta - 1),\\ \nabla_{\theta\varphi}^2\tilde n_1^{(1)} = \sin\varphi[\operatorname{ctg}\theta(\operatorname{ctg}\theta - \cos\theta) + \sin\theta]\\ -\frac{1}{\sin\theta}\left[\frac{\partial}{\partial\theta}(\tilde n_1^{(0)}\sin^2\theta) + \frac{\Delta\omega}{\eta}\frac{\partial}{\partial\varphi}\tilde n_1^{(0)}\right],\\ \nabla_{\theta\varphi}^2\tilde n_1^{(2)} = \sin\varphi\left[\left(\cos^2\theta - \frac{1}{3}\right)\operatorname{ctg}\theta\left(\frac{1}{\sin\theta} - 1\right) + \sin 2\theta\right]\\ -\frac{1}{\sin\theta}\left[\frac{\partial}{\partial\theta}(\tilde n_1^{(1)}\sin^2\theta) + \frac{\Delta\omega}{\eta}\frac{\partial}{\partial\varphi}\tilde n_1^{(1)}\right].\end{gathered} \tag{3.17}$$

The solutions of these equations take the form

$$\begin{gathered}\tilde n_1^{(0)} = \sin\varphi F_0(\theta),\\ \tilde n_1^{(1)} = \sin\varphi F_1(\theta) + \frac{\Delta\omega}{\eta}\cos\varphi\Psi_0(\theta),\\ \tilde n_1^{(2)} = \sin\varphi F_2(\theta) + \frac{\Delta\omega}{\eta}\cos\varphi\Psi_1(\theta) + \left(\frac{\Delta\omega}{\eta}\right)^2\sin\varphi\Phi_0(\theta),\end{gathered} \tag{3.18}$$

where F_i, Ψ_i, and Φ_i are functions of θ and are determined by integrating Eqs. (3.17) subject to the requirement that the solution be bounded on the interval $[0,\pi)$ (see the Appendix).

Formulas (3.18) make it possible to determine the absorption line shape by integrating (3.1). The expression obtained is valid near resonance, inasmuch as the expansion above in powers of $\mu H_0/T$ is also a series in powers of $\Delta\omega/\eta$. The condition $\Delta\omega/\eta \ll 1$, however, is not too stringent, inasmuch as $\eta \sim 10^4$ Hz.

Leaving out the cumbersome calculations, we note that the term with F_0 (as well as the equilibrium function n_0 and all the terms with $\cos\varphi$) vanishes when Eq. (3.1) is integrated. For our purpose it suffices to retain in second order only the Φ_0 term, which gives the dependence on $\Delta\omega$ (the term with F_2 yields only a small correction, expressed in terms of F_1, to the value of the resonant maximum). We ultimately have

$$\begin{gathered}\chi''(\Delta\omega) = -\frac{\mu\omega_1}{16\pi H_1}\frac{N}{f}\frac{\mu H_0}{T}\int_0^\pi\left[F_1(\theta) + \frac{\mu H_0}{T}\left(\frac{\Delta\omega}{\eta}\right)^2\Phi_0(\theta)\right]\sin^2\theta\,d\theta\\ = \frac{M^2\gamma^2NR_0^5}{36\chi_0\omega_0 D}\left(\frac{\mu H_0}{T}\right)^2\left[\left(2\pi + \frac{7}{3}\right)\ln 2 - \frac{\pi^2}{6} - \frac{5}{24}\pi - \frac{19}{6}\right.\\ \left.-\frac{\mu H_0}{T}\left(\frac{\Delta\omega}{\eta}\right)^2\left(\frac{1}{2} + \frac{\pi^2}{4}\ln 2\right)\right].\end{gathered} \tag{3.19}$$

According to (3.6), the distorting action of the FPR on the magnetization of the medium drops off slowly with distance. Each point of the paramagnet is perturbed by a set of FPR with randomly oriented moments. The averaged perturbation is negligibly small, so that the influence of FPR on one another via the paramagnetic medium can be disregarded. For the same reason we can neglect the corrections to the homogeneous absorption in the paramagnetic medium. These corrections are small also compared with (3.19), by virtue of the smallness of $\chi_0 H_0/M \ll 1$.

Strong constant field

In a strong magnetic field $\mu H_0 \gg T$ the magnetic moments of the FPR are polarized along the field. The distribution function degenerates into a constant, $n(\theta,\varphi) \to N$. The longitudinal components m_z and M_z of the magnetization vectors remain unchanged in the approximation linear in H_1 when the alternating field is turned on. Rotating transverse components are produced in this case, however. The diffusion flux through the FPR surface is so directed that the phase difference between the precessing m_+ and M_+ decreases. The absorption of the energy of the alternating magnetic field by the FPR is due to the slowing down of the precession of its magnetic moment by the diffusion flux through the surface.

The magnetization of the paramagnet is described by the Bloch equation with diffusion term. In a rotating Cartesian system CS(ω) we have [cf. (2.18) and (3.4)]

$$\dot{\mathbf{m}}=\gamma[\mathbf{m}\times\mathbf{H}_e]-\frac{m_x\mathbf{i}+m_y\mathbf{j}}{T_2}+D\nabla^2\mathbf{m}, \tag{3.20}$$

where i and j are the unit vectors of the CS(ω); $\mathbf{H}_e(-\omega_1/\gamma, 0, \Delta\omega/\gamma)$ is the effective field in the CS(ω). The spherically symmetrical stationary solution of (3.20) is of the form

$$m_+(r)=C[\exp-(\beta+ik)r]/r+m_+^{(0)} \quad (R_0<r<\infty), \tag{3.21}$$

where C is a constant determined from the boundary conditions;

$$\beta=\frac{1}{\lambda}=\left\{\frac{[1+(T_2\Delta\omega)^2]^{1/2}+1}{2DT_2}\right\}^{1/2}$$

is the reciprocal length over which the influence of the phase-inhomogeneity center (the influence of the FPR on the paramagnet attenuates);

$$k=\left\{\frac{[1+(T_2\Delta\omega)^2]^{1/2}-1}{2DT_2}\right\}^{1/2}$$

is the wave vector of the standing spherical wave;

$$m_+^{(0)}=\chi_0H_0\gamma H_1T_2(i+\Delta\omega T_2)/[1+(\Delta\omega T_2)^2]$$

is the equilibrium value of the transverse component of the magnetization vector of the homogeneous paramagnet.

We consider the case $\lambda \ll 1$. We can confine ourselves then to an isolated FPR in a paramagnetic medium. The imaginary part of the susceptibility is then given by

$$\chi''=\chi_p''+\mathcal{N}x\chi_v''+N\int_Q\chi''(r)\,d\mathbf{r}, \tag{3.22}$$

where

$$\chi_p''=\omega_0T_2\chi_0/[1+(\Delta\omega T_2)^2], \tag{3.23}$$

$$\chi_v''=-M_y/H_1, \tag{3.24}$$

$$\chi''(r)=-m_y(r)/H_1, \tag{3.25}$$

and m_y and M_y are connected by the principal boundary condition

$$M_y/M=m_y(R_0)/\chi_0H_0. \tag{3.26}$$

We determine the constant C by recognizing that the change of the magnetic moment of the FPR in the CS(ω) is determined by the precession around the direction of the effective magnetic field and by the diffusion flux of the phase of the transverse component through the surface. From the continuity equation it follows in the stationary case that

$$^4/_3\pi R_0^3\gamma[\mathbf{MH}_e]+\oint\mathbf{j}^{(n)}ds=0. \tag{3.27}$$

Substituting (3.21) in (3.27) and taking (3.26) into account, we obtain

$$C=R_0\chi_0H_0\frac{\gamma H_1}{\Delta\omega}\frac{1-iT_2\Delta\omega}{1+(T_2\Delta\omega)^2}\frac{\exp(\beta+ik)R_0}{1+3ib[(\beta+ik)R_0+1]}, \tag{3.28}$$

$b=\chi_0H_0D/MR_0^2\Delta\omega$. Using formula (3.28), we easily obtain the line shape (3.22). In view of the complexity of the expression, we write down only the dependence of the signal at resonance on the FPR density:

$$\chi''(x)=\omega_0T_2\chi_0(1+\mathcal{N}xM/2\chi_0H_0). \tag{3.29}$$

In the opposite case $\lambda \gg l$ the mutual influence of the FPR via the paramagnetic medium (this influence is not made to vanish by the averaging, owing to the identical orientations of the magnetic FPR) can be taken into account in the mean-field approximation. The change of the space-averaged (and by the same token, coordinate-independent) magnetization of the paramagnet is described by the Bloch equation, and the change of the FPR magnetization is described by the free-precession equation. The connection between the FPR and the medium is given by

$$\dot{\mathbf{m}}=-^4/_3\pi NR_0^3\dot{\mathbf{M}}, \tag{3.30}$$

and the self-consistency of the calculation lies in the boundary condition (3.26). It is easy to obtain from the foregoing an expression for the imaginary part of the susceptibility as the sum of expressions (3.24) and (3.25):

$$\chi''=\frac{\chi_0\omega_0T_2(1+\mathcal{N}xM/\chi_0H_0)^2}{1+[\Delta\omega T_2(1+\mathcal{N}xM/\chi_0H_0)]^2}. \tag{3.31}$$

4. CONCLUSION

The correlation time (2.13) for the vacancion relaxation processes at $T\sim1.5$ K is $\tau_c\sim10^{-8}$ sec, thus justifying the use of the short-relaxation-time approximation (the conditions $T_1\gg c$, $T_2\gg c$, and $\overline{\mathscr{H}}_d\tau_c\ll1$). With decreasing temperature and with exponential decrease of the vacancy density, the vacancion regime "freezes out" and a transition takes place, within a time $\tau_c\sim I^{-1}\sim10^{-6}$ sec, to a regime in which the relaxation is determined by the tunneling of the nuclear spins themselves, thereby modulating the dipole-dipole interaction.

In principle, relaxation is also possible on account of dipole-dipole interaction of the magnetic moments of the FPR and the He^3 nuclei in a paramagnetic region. An estimate (Ref. 7, Chap. VIII), however, yields $T_1\sim T_2\sim10^4$ sec. Thus, an FPR ensemble relaxes very slowly: $T_2'\gg T_2$. Actually the line of the FPR subsystem should broaden just the same, on account of collisions with phonons, but at $T\sim1$ K, in view of the smallness of $x\mathcal{N}_2\ll1$, this line cannot be discerned at all against the background of the broad line of the paramagnetic medium with T_2 from Eq. (2.17).

Absorption that might be separable in an FPR system from the homogeneous absorption (3.23) in a paramagnet, would be observed if vacancy density $x\sim10^{-4}$ were produced at low temperatures $T\sim10^{-2}$ K. The thermal change of the orientation of the FPR magnetic moment, which is possible in a field $H\sim10^2$ G, manifests itself in the temperature dependence of the line shape (3.19). The resonance maximum is in this case (assuming $\chi_0(T\sim10^{-2}\text{ K})\sim10^{-6}$, Ref. 10) to be $\chi''\sim\chi_p''\sim10^{-3}$.

More convenient from the point of view of the analysis of the experimental data is the case of a strong magnetic field ($H>10^3$ G at $T\sim10^{-2}$ K). On approaching resonance, λ tends to its maximum value $\lambda_0\sim10^{-4}$ cm. Near resonance, the transition from the regime $\lambda\ll l$ to $\lambda\gg l$ [formulas (3.29) and (3.31)] occurs at densities $x\sim10^{-10}$. The lowest densities needed to observe the renormalization of T_2 [see (3.29)] and of the amplitude of the resonant absorption [(3.29) and (3.31)] depend on the concrete experimental condition. The $\chi''(x)$ dependence makes it possible to monitor the vacancy density in the crystal, a factor that can be of use in the corresponding nonequilibrium experiments.

High temperature NMR experiments lend themselves easily to treatment with participation of FPR (Sec. 2) and yield quite reasonable values for their characteristics. Much attention is currently paid to NMR in the low-temperature region. It would be of interest to extend the scope of this research by performing experiments in the vacancion regime, i.e., accompanied by production of nonequilibrium vacancy densities. The results of Sec. 3 provide for this regime a theoretical description that can be used also in the search for zero vacancies.

I am deeply grateful to A. F. Andreev for attentive guidance and valuable advice, and to V.I. Marchenko for a helpful discussion.

APPENDIX

Taking into account the discussion, in Sec. 3, of the solutions of Eqs. (3.17), we write down in explicit form only those functions F_i, Ψ_i, and Φ_i, which are needed for the calculation of the imaginary part of the susceptibility (3.19):

$$F_0(\theta)=\frac{1}{\sin\theta}\left[\frac{\pi}{2}-\left(\frac{\pi}{2}+\ln 2-\ln\sin\theta\right)\cos\theta-\theta-\ln\operatorname{tg}\frac{\theta}{2}\right], \quad (A.1)$$

$$\begin{aligned}F_1(\theta)=&\frac{1}{\sin\theta}\biggl\{\pi+\left(1-\frac{\pi}{2}\right)\ln 2-\frac{1}{2}\ln^2 2-\frac{\pi^2}{6}\\&+\cos\theta\left[\theta+\frac{\pi}{2}(\ln 2-1)+\frac{\pi^2}{6}-\frac{1}{2}\ln^2 2\right]-2\sin\theta\\&-\cos^2\theta\left(\ln\sin\theta+\frac{\pi}{2}+\ln 2\right)+\frac{1}{2}(1+\cos\theta)\ln^2(1+\cos\theta)-\ln(1+\cos\theta)\\&+\cos\theta\ln\sin\theta\left[2\cos\theta+\frac{\pi}{2}-\ln(1+\cos\theta)\right]+\ln\operatorname{tg}\frac{\theta}{2}\biggl[\ln\sin\theta\\&+\theta-1-\frac{\pi}{2}-\left(\frac{\pi}{2}+\ln 2\right)\cos\theta\biggr]-\ln^2\sin\theta+\left(\frac{\pi}{2}+\ln 2\right)\ln\sin\theta\\&-\int\ln\operatorname{tg}\frac{\theta}{2}\,d\theta-\cos\theta\int\frac{\ln(1+\cos\theta)}{1-\cos\theta}\,d\cos\theta-\cos\theta\int\theta\operatorname{ctg}\theta\,d\theta\biggr\},\end{aligned} \quad (A.2)$$

$$\begin{aligned}\Phi_0(\theta)=&\frac{1}{\sin\theta}\biggl\{\frac{\pi}{2}\biggl[1+\frac{\pi^2}{4}-\frac{\pi}{3}+\left(\frac{\pi}{2}-1\right)\ln 2\biggr]\\&-\frac{1}{2}\ln^2 2+\biggl[\left(\pi-1+\frac{1}{2}\ln 2\right)\ln 2+\frac{\pi^2}{3}+\frac{\pi}{2}\left(1-\frac{\pi}{2}\right)\ln 2\\&-\frac{\pi}{2}-\frac{\pi^3}{8}\biggr]\cos\theta+\left[\ln\operatorname{tg}\frac{\theta}{2}-\frac{\pi}{2}\left(1-\frac{\pi}{2}-\ln 2\right)\right]\sin\theta\\&+\left(1-\ln 2-\frac{\pi}{2}+\ln\sin\theta\right)\theta\sin\theta+(1-\ln 2)\biggl(\ln\operatorname{ctg}\frac{\theta}{2}\\&+\cos\theta\ln\sin\theta\biggr)+\theta\left[\left(1-\frac{\pi}{2}\right)\left(\frac{\pi}{2}+\ln 2\right)-\ln\sin\theta-1\right]\\&-\frac{\pi}{2}(1+\cos\theta)\ln(1+\cos\theta)-\frac{1-\cos\theta}{2}\ln(1+\cos\theta)\ln(1-\cos\theta)\\&+(2-\sin\theta)\int\theta\operatorname{ctg}\theta\,d\theta-\cos\theta\int\frac{\theta\,d\theta}{\sin\theta}+\int\frac{\ln(1-\cos\theta)}{1+\cos\theta}\,d\cos\theta.\end{aligned} \quad (A.3)$$

[1] R. A. Guyer, R. C. Richardson, and L. I. Zane, Rev. Mod. Phys. **43**, 532 (1971).
[2] A. F. Andreev, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 608 (1976) [JETP Lett. **24**, 564 (1976)].
[3] S. V. Iordanskiĭ, *ibid.* **26**, 183 (1977) [**26**, 171 (1977)].
[4] H. A. Reich, Phys. Rev. **129**, 630 (1962).
[5] R. C. Richardson, E. Hunt, and H. Meyer, Phys. Rev. **A138**, 1326 (1965).
[6] N. Sullivan, G. Deville, and A. Landesman, Phys. Rev. **B11**, 1858 (1975).
[7] A. Abragam, Principles of Nuclear Magnetism, Oxford, 1960.
[8] L. L. Buishvili and A. I. Tugushi, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 86 (1977) [JETP Lett. **26**, 78 (1977)].
[9] A. E. Meĭerovich, *ibid.* **25**, 485 (1977) [**25**, 453 (1977)].
[10] E. D. Adams, J. M. Delrieuv and A. Landesman, J.Phys. Lett. **39**, L-190 (1978).

Translated. by J. G. Adashko

Heat capacity of $Pt_3Mn_xFe_{1-x}$ alloys

N. I. Kourov, S. M. Podgornykh, Yu. N. Tsiovkin, and N. V. Volkenshteĭn

Institute of Metal Physics, Ural Scientific Center, USSR Academy of Sciences

(Submitted 7 May 1980)
Zh. Eksp. Teor. Fiz. **79**, 1921–1926 (November 1980)

The adiabatic-calorimeter method is used to investigate experimentally the heat capacity of the atomically ordered alloys $Pt_3Mn_xFe_{1-x}$ ($x=0$, 0.2, 0.3, 0.4, 0.5, 0.8, 1) in the temperature interval 13–300 K. The alloys are antiferromagnetic at $x=0$ and ferromagnetic at $x=1$. The temperature and concentration dependences of the magnetic part of the heat capacity are discussed within the framework of the model of the nucleation mechanism of a concentration phase transition.

PACS numbers: 65.40.Em

It was shown by a number of workers[1,2] that a ferromagnetic-antiferromagnetic phase transition is produced in quasibinary solid solutions based on the atomically ordered Pt_3Mn–Pt_3Fe alloys when the concentration of the magnetic components is varied at low temperatures. The initial alloys have at room temperature an fcc lattice with close parameters: $a=3.89$ Å, for the Pt_3Mn alloy and $a=3.87$ Å for the Pt_3Fe alloy. In the antiferromagnetic state at $T\leqslant T_N=164$ K the lattice of the Pt_3Fe alloy becomes weakly tetragonal ($c/a=0.9998$). The Pt_3Mn alloy is a collinear ferromagnet at $T\leqslant T_c$ ($T_c=390$ K).

The solid solutions $Pt_3Mn_xFe_{1-x}$ have at manganese