NMR AND ORIENTATIONAL PHASE TRANSITIONS IN ORTHOFERRITES

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A method based on symmetry theory is proposed for the determination of the anisotropy of the hyperfine field in magnetically ordered crystals. The temperature dependence of the NMR frequencies following spin reorientation in orthoferrites is considered. The behavior of the NMR frequencies in orientational phase transitions is considered on the basis of the magnetic phase diagram of the orthoferrite.

We shall consider the behavior of the NMR frequencies in orientational transitions. To this end, we determine the connection between the hyperfine fields acting on the investigated Fe^{57} nuclei with electronic magnetizations. It is convenient to determine this connection from symmetry theory.

1. Let $\vec{M}_i$ (i = 1, 2, 3, 4) the magnetization of the i-th iron sublattice and let $\vec{h}_i$ be the hyperfine field acting on the nuclei of the i-th sublattice. It is known that the following combinations [1]

$$\begin{aligned} \mathbf{F} &= \mathbf{M}_1 + \mathbf{M}_2 + \mathbf{M}_3 + \mathbf{M}_4, \quad \mathbf{A} = \mathbf{M}_1 - \mathbf{M}_2 - \mathbf{M}_3 + \mathbf{M}_4, \\ \mathbf{G} &= \mathbf{M}_1 - \mathbf{M}_2 + \mathbf{M}_3 - \mathbf{M}_4, \quad \mathbf{C} = \mathbf{M}_1 + \mathbf{M}_2 - \mathbf{M}_3 - \mathbf{M}_4 \end{aligned} \tag{1}$$

transform in accordance with one-dimensional irreducible representation of the orthoferrite space group (see the table). It is easy to verify that the following cominations are also transformed:

$$\begin{aligned} \mathbf{f} &= \mathbf{h}_1 + \mathbf{h}_2 + \mathbf{h}_3 + \mathbf{h}_4, \quad \mathbf{a} = \mathbf{h}_1 - \mathbf{h}_2 - \mathbf{h}_3 + \mathbf{h}_4, \\ \mathbf{g} &= \mathbf{h}_1 - \mathbf{h}_2 + \mathbf{h}_3 - \mathbf{h}_4, \quad \mathbf{c} = \mathbf{h}_1 + \mathbf{h}_2 - \mathbf{h}_3 - \mathbf{h}_4. \end{aligned} \tag{2}$$

	M_i			h_i		
Γ_1	F_x	G_z	C_y	f_x	g_z	c_y
Γ_2	F_y	A_z	C_x	f_y	a_z	c_x
Γ_3	F_z	G_x	A_y	f_z	g_x	a_y
Γ_4	G_y	A_x	C_z	g_y	a_x	c_z

Our problem is to obtain a linear rleation between $\vec{h}_i$ and $\vec{M}_i$. It is obvious that linear relations can occur only between those components of $\vec{h}_i$ and $\vec{M}_i$ which transform in accordance with the same irreducible representation.

We turn to the two-sublattice approximation ($\vec{A} = \vec{C} = 0$). We assume also that $\vec{a} = \vec{c} = 0$. We then have in accordance with the table

$$\begin{aligned} f_x &= a_1 F_x + a_2 G_z, \quad g_z = a_3 F_x + a_4 G_z, \quad f_y = a_5 F_y, \\ f_z &= a_6 F_z + a_7 G_x, \quad g_x = a_8 F_z + a_9 G_x \quad g_y = a_{10} G_y. \end{aligned}$$

Alternately, going over to fields $\vec{h}_{1,2} = \vec{f} \pm \vec{g}$, we obtain:

$$\mathbf{h}_{1,2} = \begin{pmatrix} a_1 & 0 & \pm a_8 \\ 0 & a_5 & 0 \\ \pm a_3 & 0 & a_6 \end{pmatrix} \mathbf{F} + \begin{pmatrix} \pm a_9 & 0 & a_2 \\ 0 & \pm a_{10} & 0 \\ a_7 & 0 & \pm a_4 \end{pmatrix} \mathbf{G}, \tag{3}$$

where the ± signs and the subscripts 1 and 2 pertain to two non-equivalent positions of the iron ions in the crystal.

2. We examine the behavior of the NMR frequency following a spin reorientation that occurs in the ac plane of the crystal. We put $F_x = F \sin\theta$, $F_z = F \cos\theta$, $G_x = G \cos\theta$, and $G_z = G \sin\theta$.

Then

$$(h_{1,2})_x = b_1 \sin\theta \pm b_2 \cos\theta, \quad (h_{1,2})_y = 0, \quad (h_{1,2})_z = \pm b_3 \sin\theta + b_4 \cos\theta. \tag{4}$$

The hyperfine parameters b_1, b_2, b_3, and b_4 depend on F and G, and can be regarded as constant if the magnetic field is not too strong (H << d where d is the Dzyaloshinskii field).

The spin of the Fe^{57} nucleus is I = 1/2; its NMR frequencies are $\omega_{1,2} = \gamma_n |\vec{h}_{1,2}|$. Using (4), we obtain

$$\omega_{1,2} = \gamma_n [b_1^2 + b_3^2 + (b_2^2 + b_4^2 - b_1^2 - b_3^2)\cos^2\theta \pm (b_1 b_2 + b_3 b_4)\sin 2\theta]^{1/2} \tag{5}$$

Substituting in (5) the known form of $\theta(T)$ [2], we obtain

$$\omega_{1,2} = \begin{cases} \omega_1 \equiv \gamma_n (b_2^2 + b_4^2)^{1/2}, & T > T_1 \\ \left[\omega_2^2 + (\omega_1^2 - \omega_2^2)\dfrac{T - T_2}{T_1 - T_2} \pm 2\gamma_n^2 (b_1 b_2 + b_3 b_4)\dfrac{(T_1 - T)^{1/2}(T - T_2)^{1/2}}{T_1 - T_2}\right]^{1/2}, & T_2 < T < T_1 \\ \omega_2 \equiv \gamma_n (b_1^2 + b_3^2)^{1/2}, & T < T_2 \end{cases} \tag{6}$$

where T_2 and T_1 are the temperatures of the beginning and end of the reorientation. This formula agrees with the experimental results of [3].

3. We investigate the influence of the magnetic field H on the NMR frequencies at temperatures close to the reorientation temperature (in the ac plane).

Let H ∥ C; then the NMR frequencies are given by

$$\omega_{1,2} = \gamma_n |\mathbf{h}_{1,2} + \mathbf{H}| = [(\omega_{1,2}^0)^2 + (\gamma_n H)^2 + 2\gamma_n^2 H^2 (\pm b_3 \sin\theta + b_4 \cos\theta)]^{1/2}, \tag{7}$$

where $\omega_{1,2}^0$ is determined by formula (5).

To analyze the behavior of the NMR frequencies, we use the phase diagram of an orthoferrite near the reorientation region [4]. In the simplest case, it can be obtained by minimizing the free energy

$$F(\theta) = \frac{K_1(T)}{2}\sin^2\theta + \frac{K_2}{4}\sin^4\theta - mH\cos\theta, \quad K_1(T) = K\frac{T - T_1}{T_1},$$

$$K > 0, \quad K_2 > 0.$$

The results of the minimzation are the following (see Fig. 1).

1. The phases θ_I. Its stability-loss line T_1B is determined by the equation $K_1(T)+mH = 0$.

2. The angle phase θ_{II}. The angle θ is given by the rleation

$$\cos\theta = \begin{cases} 2r \operatorname{sh}\dfrac{1}{3} \operatorname{arc\,sh} {}^{q}/_{r^3}, & T < T_2 \\ 2r \operatorname{ch}\dfrac{1}{3} \operatorname{arc\,ch} {}^{q}/_{r^3}, & T_2 < T < T_1, \quad r^3 < |q|, \\ 2r \cos\left(\dfrac{\pi}{3} - \dfrac{1}{3} \arccos {}^{q}/_{r^3}\right), & T_2 < T < T_1, \quad r^3 > |q| \end{cases} \tag{8}$$

where

$$r = (|K_1 + K_2|/3K_2)^{1/2}, \quad q = -\frac{mH}{2K_2}.$$

On the line T_1B, the angle phase goes over continuously into the phase $\theta_I = 0$.

3. The metastable phase $\theta_{III} = \pi$. It is stable in the region bounded by the line TT_1A; the equation of the line T_1A is $K_1(T) = mH$.

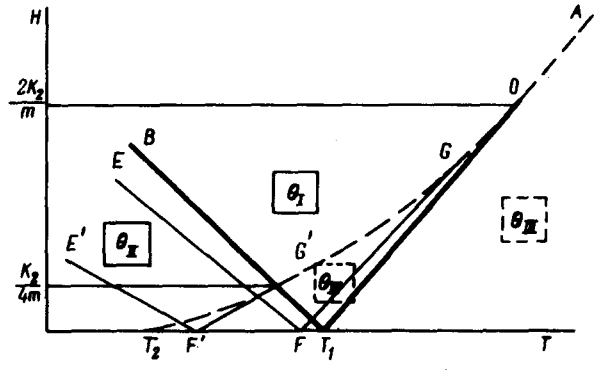

Fig. 1

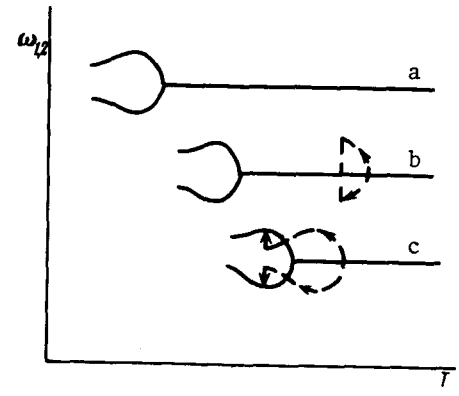

Fig. 2

Fig. 1. Magnetic phase diagram of rare-earth orthoferrite near the reorientation temperature (H ∥ C).

Fig. 2. Schematic representation of the possible temperature dependences of the NMR frequencies in spin reorientation. The frequency splittings represented by the dashed curves can appear only during cooling (at H ∥ c). a - $H > 2K_2/m$, b - $K_2/4m < H < 2K_2/m$, c - $H < 2K_2/m$.

4. The metastable angle phase θ_{IV}. The equation for θ is

$$\cos\theta = -2r\cos\left(\frac{1}{3}\operatorname{arc}\cos{}^{q}/_{r^3}\right).$$

On the T_1O line, the phase θ_{III} goes over continuously also into the metastable phase θ_{IV}. This transition can be realized because the metastable phase θ_{III} is separated from the stable phase θ_I on line T_1O by an energy barrier. The line T_2O is the stability-loss (spinodal) line of the phase θ_{IV}. It is the envelope of a family of equal-angle curves, and its equation is

$$\left(\frac{K_1 + K_2}{3K_2}\right)^3 + \left(\frac{mH}{2K_2}\right)^2 = 0 \qquad (10)$$

The discontinuity of the angle θ on the line T_2O can be determined from (9) by substituting (10) in (9). The point O (the analog of a triple critcal point) has the coordinates $T_0 = T_1[1 + (3K_2/K)]$ and $H_0 = 2K_2/m$.

Let us examine the possible transitions that occur in a given magnetic field when the temperature is varied. The following modes are possible:

I. Upon cooling, the stable phase θ_I always goes over into the stable phase θ_{II} on the line BT_1. This is a reversible transition.

II. The transition from the metastable phase θ_{III} can proceed differently, depending on the magnetic field:

a) $H > 2K_2/m$. Upon cooling the phase θ_{III} goes over on line OA jumpwise into θ_I, after which the behavior is as in mode I.

b) $K_2/4m < H < 2K_2/m$. On cooling we have $\theta_{III} \to \theta_{IV}$ (continuously on line OT_1), $\theta_{IV} \to \theta_I$ (jumpwise on line T_2O), and from then on as in mode I.

c) $H < K_2/4m$. On cooling $\theta_{III} \to \theta_{IV}$ (continuously on OT_1), $\theta_{IV} \to \theta_{II}$ (jumpwise on T_2O), and then as in mode I.

All the foregoing pertains to homogeneous systems. In real systems, the metastable phases can exist in the form of domains. In this case the regions of existence of these phases on Fig. 1 are regions of possible existence of such domains.

Using the considered transition schemes, expressions (8) and (9) for the angles $\theta(T)$, and formula (7) for $\omega_{1,2}$, we can plot the temperature dependences of the NMR frequencies. They are shown schematically in Fig. 2 for the following relations between the hyperfine parameters:

$b_2 \sim b_3 \sim \omega_1/\gamma$, $b_1 \sim b_4 \sim 10^{-2}\omega_1/\gamma$, and $H_0 < b_1$.

To analyze the behavior of the frequencies at H a it is necessary to use the appropriate phase diagram [4].

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STABILIZATION OF NITROGEN ATOMS IN SUPERFLUID HELIUM

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It is shown that the stationary concentration of nitrogen atoms that are stabilized in superfluid helium exceeds 1.6%. The peculiariites of the recombination radiation have made it possible to estimate the recombination activation energy at 0.1 kcal/mole and to advance the hypothesis that solid nitrogen granules experience thermal explosion on going through the λ point.

The purpose of the present paper was to ascertain whether the recombination of atoms is an activated process (i.e., whether its realization calls for a supply of heat from the outside) and consequently determine whether it is possible, at least in principle, to stabilize large concentrations of atoms when the temperature approaches absolute zero. In the past, many experiments aimed at freezing atoms from a discharge on a substrate at 4.2°K (see the reviews [1, 2]) have led to the conclusion that the concentrations of the stabilized atoms doe not exceed several tenths of one per cent. Similar results were obtained in experiments on radiative accumulation of atoms in solid molecular substances [1 - 3]. The developed theories [4 - 8] connected the existence of a limiting concentration atoms with instability to thermal explosion (the recombination process was assumed to be non-activated, and the diffusion of the atoms in the matrix was assumed to be activated). Analysis has shown, however, that the experiments described in the literature were performed at temperatures on the order of several times 10°K: at the instant of deposition, the temperature of the substrate increased to about 20°K [2]; an even higher temperature was possessed by the "hot points" in the case of radiative accumulation [1 - 3]. A significant lowering of the temperature in the region of intense sticking together of the atoms can lead to an appreciable increase of their stationary concentrations, both as a result of stabilization of the atoms in shallower traps of the matrix, and as a result of the appearance of a hypothetical activation energy of the recombination process.

Within the known procedures, it is impossible in principle to lower the temperature appreciably in the region of intense sticking. We have therefore decided to introduce the atoms in the form of a beam into the interior of cooled liquid helium, through its serface. Such a method would make it possible immediately (i) to lower the observation temperature to 1.2 - 1.5 K, (ii) thermalize the atoms before the arrive into the region of intense sticking, (iii) ensure the possibility of working with larger fluxes (10^{20} particles per second and more), owing to the effective heat removal in the superfluid helium.

To realize this method it was absolutely essential to produce a directional beam that reached directly the surface of the liquid; otherwise the atoms would be carried away by the intense rising flow of evaporating helium. Quite unexpectedly, the outflow of the warm (100 - 200°K) gas from a small opening into cold (1.5 - 3.0°K) helium gas under the influence of small pressure gradients ($\Delta P \simeq P_{He}$) leads to the formation of a strongly pronounced beam. The