

# Absorption of the energy of low-frequency electromagnetic or sound fields by non-Kramers $\text{Ho}^{3+}$ ions in $\text{CaWO}_3$ single crystals

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Results are reported of an investigation of the absorption of the energy of low-frequency electromagnetic and acoustic fields by a system of non-Kramers  $\text{Ho}^{3+}$  ions in a  $\text{CaWO}_3$  matrix. It is observed that in an external magnetic field corresponding to the intersection points of the hyperfine sublevels of the  $\text{Ho}^{3+}$  ions the field dependence of the absorption has local singularities. It is demonstrated experimentally and theoretically that the effect is due principally to Orbach-Aminov relaxation processes at 4.2 K, and to direct transitions between the energy levels at the points of their intersection at 1.6 K. Comparison of the theory with experiment yielded estimates of the constants  $\Delta$ ,  $A_{\pm}$ , and  $B$  of the spin Hamiltonian, of the distance  $\delta$  to the nearest excited Stark level of the  $\text{Ho}^{3+}$  ion, of the spread  $\gamma$  of the dipole fields, of the rate of relaxation due to the direct or Orbach processes, as well as of the spin-phonon coupling constant, which turned out to be somewhat larger than expected. It is noted that the distinctive structure of the  $\text{Ho}^{3+}$  ion energy levels in crystals with Scheelite structure makes the low-frequency procedure highly informative.

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## 1. INTRODUCTION

In a search for nuclear acoustic resonance signals of  $\text{Tm}^{3+}$  ions in the van Vleck paramagnet  $\text{LiTmF}_4$  we observed four intense longitudinal ultrasound-absorption signals at  $\sim 10$  MHz, which were found to be due to the presence of a non-Kramers  $\text{Ho}^{3+}$  ion impurity of very low density in the crystal. We registered also energy-absorption lines from a low-frequency electromagnetic field, where the  $\text{Ho}^{3+}$  ions interacted with the magnetic-field component parallel to the external constant magnetic field (we shall refer hereafter, for brevity, simply to absorption of the alternating-magnetic-field energy). If it is recognized that the study of certain non-Kramers ions by resonance methods in the microwave band entails certain difficulties (the EPR lines are symmetrically broadened by strong spin-photon interactions and by local lattice distortions), our interest in the observed phenomenon becomes understandable.

The van Vleck paramagnet  $\text{LiTmF}_4$  has a very large magnetostriction effect,<sup>1</sup> which hinders greatly investigations of ultrasound absorption. In addition, the  $\text{Ho}^{3+}$  ion density in the investigated sample was too small for a reliable observation of alternating magnetic field energy absorption lines. We chose therefore to investigate single-crystal  $\text{CaWO}_3:0.5 \text{ at.}\% \text{ Ho}^{3+}$ , which has the same crystal structure as  $\text{LiTmF}_4$  (local symmetry  $S_4$ ) but is free of the indicated shortcomings.

The very first experiments yielded unexpected and at first glance not properly understood results. It seemed that negative absorption of the electromagnetic energy appears in the spin system at certain values of the longitudinal external magnetic field component when the temperature is raised from 1.6 to 4.2 K, and at other values when a transverse component appears. It will be made clear below that the entire set of the experimental results can be described, at least qualitatively within the framework of the theoretical approach developed by us.

## 2. SPIN HAMILTONIAN AND ENERGY LEVELS

The Hamiltonian that describes the states of a non-Kramers ion with a definite total magnetic moment  $J$  can be written in the form

$$\mathcal{H}_i = \mathcal{H}_{cr}^0(J) + \Delta \mathcal{H}_{cr}(J) + \mathcal{H}_z(J) + \mathcal{H}_{hf}, \quad (1)$$

where  $\mathcal{H}_{cr}^0(J)$  describes the energy of the interaction of the ion with the crystal field of basic symmetry,  $\Delta \mathcal{H}_{cr}(J)$  is due to the local distortions of the symmetry,  $\mathcal{H}_z = g_J \beta(HJ)$  is the Zeeman energy in the magnetic field, and  $\mathcal{H}_{hf} = A(JI)$  is the hyperfine interaction with the nuclear spin  $I$ . Here  $g_J = \frac{5}{4}$  is the Landé factor and  $A = +812.1$  MHz is the hyperfine-interaction constant of the free ion.<sup>2</sup>

A crystal field of local symmetry  $S_4$  splits the ground multiplet of the  $\text{Ho}^{3+}$  ion ( $f^{10}, {}^5I_8$ ) in such a way that the lower state is a non-Kramers doublet split by the hyperfine interaction into 8 sublevels ( $I = \frac{7}{2}$ ). A singlet is located at a distance  $\delta \approx 9 \text{ cm}^{-1}$  from the doublet, and the states above are singlets and doublets. The Hamiltonian (1), projected on the doublet states in the usual manner but with account taken of the terms of second order in  $\mathcal{H}_i - \mathcal{H}_{cr}^0(J)$ , is expressed in terms of the effective spin  $S = \frac{1}{2}$  in the form

$$\mathcal{H}_i = g_{\parallel} \beta S_z H \cos \theta + A_{\pm} S_z I_z + \Delta_{\pm} S_{\pm} + \Delta_{\pm} S_{\mp} + A_{\pm} (I_{\pm} S_{\pm} + I_{\mp} S_{\mp}) + B(S_{\pm} I_{\pm}^2 + S_{\mp} I_{\mp}^2), \quad (2)$$

where the  $z$  axis is parallel to the  $C_4$  axis of the undistorted complex,  $\theta$  is the angle between the  $z$  axis and the external magnetic field,  $I_{\pm}$  and  $I_z = I_x \pm iI_y$  are the nuclear-spin operators,  $S_{\pm}$  and  $S_z = S_x \pm iS_y$  are the operators of the effective electron spin (the states  $\pm \frac{1}{2}$  corresponds to the doublet states  $|\xi_0\rangle$  and  $|\bar{\xi}_0\rangle$ , which are conjugate according to Kramers), and the presence of terms containing  $\Delta_{\pm} = \frac{1}{2}(\Delta_x \pm i\Delta_y)$  is due to random local distortions of the symmetry  $S_4$  of the crystal field, which are distributed about zero in accord of a certain, say Gaussian, law:

$$P(\Delta^2) = \Delta_0^{-2} \exp(-\Delta^2 / \Delta_0^2), \quad \Delta^2 = \Delta_x^2 + \Delta_y^2.$$

The experimentally obtained parameters  $g_{\parallel} = 13.69$ ;  $A_{\parallel} = 0.299 \text{ cm}^{-1}$ ;  $\Delta_0 = 0.03 \text{ cm}^{-1}$  were taken from Ref. 4.

The last two terms of (2) are small and do not influence the ESR spectrum; they are therefore not taken into account in ESR investigations of non-Kramers ions.  $A_{\perp}$  and  $B$  can be estimated by using perturbation theory for the degenerate levels<sup>5</sup> up to second order in  $\mathcal{H}_i - \mathcal{H}_{cr}(J)$  inclusive:

$$A_{\perp} = -\frac{A}{6} \langle \xi_0 | \Delta \mathcal{H}_{cr}(J) + g_{\parallel} \beta (H_x J_x + H_y J_y) | s \rangle \langle s | J_+ | \xi_0 \rangle + \text{c.c.} \rangle, \quad (3)$$

$$B = -\frac{A^2}{6} \langle \xi_0 | J_+ | s \rangle \langle s | J_+ | \xi_0 \rangle. \quad (4)$$

We have confined ourselves for simplicity in second order to the singlet state  $|s\rangle$  closest to the ground doublet and retained only the spin-Hamiltonian terms that have matrix elements missing from first-order perturbation theory.

The energy-level scheme determined by the first two terms of the spin Hamiltonian (2), which are larger than the remaining ones, is shown in Fig. 1a. The remaining terms can be accounted for by perturbation theory.

### 3. PROCEDURE AND EXPERIMENTAL RESULTS

The experiment was performed at temperatures 1.6–4.2 K. The energy absorbed from the alternating magnetic field of frequency 5–8 MHz was registered with Pound-Knight-circuit autodyne. The energy of the ~10 MHz ultrasound field was registered with an auto-

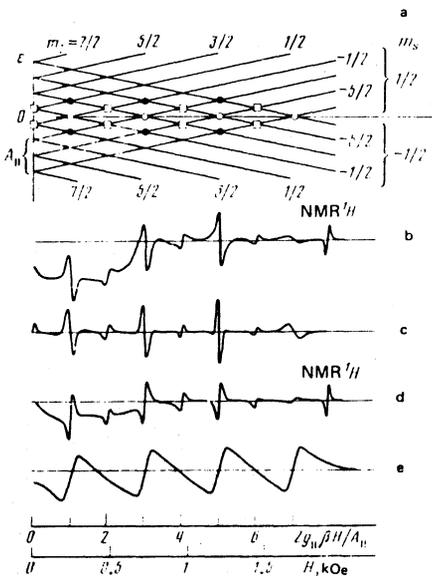


FIG. 1. a) Energy levels of  $\text{Ho}^{3+}$  ion in  $\text{CaWO}_4$  single crystal in a magnetic field parallel to the  $C_4$  axis at  $\Delta m_I = 0$  ( $\circ$ ),  $\Delta m_I = 2$  ( $\bullet$ ) and  $\Delta m_I = 1$  ( $\square$ ). b, c, d) Derivative of the absorption of the energy of an alternating magnetic field parallel to the  $C_4$  axis of the crystal at  $H \parallel C_4$ : b)  $T = 4.2 \text{ K}$ , c)  $T = 4.2 \text{ K}$ , theoretical curve, d)  $T = 1.6 \text{ K}$ . e) Derivative of the ultrasound-energy absorption at  $H \parallel C_4$ ,  $T = 4.2 \text{ K}$ .

dyne oscillator based on the Sadykov circuit.<sup>6</sup> The sample measuring  $10 \times 10 \times 5 \text{ mm}$  was an acoustic resonator with an axis parallel to the  $C_4$  axis of the crystal. The longitudinal ultrasound wave was excited at one of the overtones of the acoustic resonator with the aid of an X-cut quartz piezoelectric converter secured to the sample with a silicone oil. The measured ultrasound velocity was  $v \approx (4.67 \pm 0.05) \times 10^5 \text{ cm/sec}$ . The absorption spectra were recorded by using rectangular modulation of the magnetic field with a total amplitude swing 10 Oe and frequency 17 Hz.

Figure 1b shows the derivative of the spectrum of energy absorption from an alternating magnetic field parallel to the  $C_4$  axis, at  $H \parallel C_4$  and  $T = 4.2 \text{ K}$ . On the right side is plotted the NMR signal of the proton contained in the control sample. Absorption lines were observed in fields corresponding to  $2g_{\parallel}\beta H_x/A_{\parallel} = 2, 4, 6$ , while lines at the points  $2g_{\parallel}\beta H_x/A_{\parallel} = 1, 3, 5, 7$  have the appearance of alternating-magnetic-field emission energy lines. The lines widths between the inflection points are  $\Delta H_1 \approx 24 \pm 3$ ;  $\Delta H_3 \approx 23 \pm 3$ ;  $\Delta H_5 \approx 17 \pm 3$ ;  $\Delta H_7 \approx 60 \pm 3$ ;  $\Delta H_2 \approx \Delta H_4 \approx \Delta H_6 \approx 25 \pm 3 \text{ Oe}$ . When the angle  $\theta$  between the  $C_4$  axis and the external magnetic field is increased, the absorption lines at points 2, 4, and 6 turn into emission lines (Fig. 2).

At  $H \parallel C_4$  the emission lines at points 2, 3, 5, and 7 turn very rapidly into absorption lines as the temperature is lowered. The temperature dependence of the amplitude of these lines, measured in proton NMR absorption units in a control sample, will be discussed in detail later. We note here that the absorption varies strongly in the interval 4.2–2.0 K but remains practically constant at temperatures 2.0–1.6 K. The line amplitude was measured at a rectangular magnetic-field amplitude modulation having a swing larger than the line width. This modulation method is known<sup>7</sup> to permit registration of the absorption line itself, and not of its derivative. The shape of the derivative of the spectrum at  $T = 1.6 \text{ K}$  is shown in Fig. 1d.

The presence of emission lines in the spectrum is physically difficult to understand, since no population inversion of the spin levels was produced in the system. We have therefore attempted to observe not the derivative of the absorption spectrum, but the field dependence of the absorption (of the amplitude of the autodyne oscillations) without modulating the field. Although

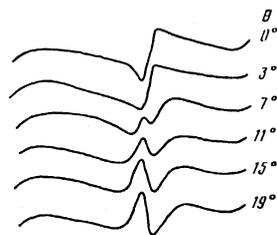


FIG. 2. Transformation of the maximum of the absorption of the alternating-magnetic field energy at the point corresponding to  $2g_{\parallel}\beta H_x/A_{\parallel} = 4$  at  $T = 4.2 \text{ K}$  into a minimum when the angle  $\theta$  is increased.

one could hardly expect a large signal/noise ratio, the latter was sufficient to establish the following: With increasing magnetic field, the absorption increases monotonically, as is incidentally seen also from Fig. 1, and local maxima and minima of the absorption are observed against the background of this absorption. Naturally, in the case of differential passage, especially at low magnetic-field modulation amplitude, these maxima and minima look respectively like absorption and "emission" lines.

The interaction of longitudinal ultrasound with the spin system of the Ho<sup>3+</sup> ions takes place only at the points 1, 3, 5, and 7, where ultrasound-absorption maxima are observed. The derivative of the absorption spectrum of ultrasound propagating along C<sub>4</sub> at H||C<sub>4</sub> and T = 4.2 K is shown in Fig. 1e. The width of the absorption lines between the inflection points is 110 ± 10 Oe, and the ultrasound absorption coefficient is δ ≈ 10<sup>-5</sup> cm<sup>-1</sup>.

#### 4. THEORY

In Fig. 1a are singled out the intersection points of the levels whose wave functions are connected with any one of the three last terms of the Hamiltonian (2). At a specified value of H, the stationary states of the Hamiltonian can be numbered by the integer index α (-8 ≤ α ≤ 8, α ≠ 0) such that an increase of α corresponds to an increase of the energy of the state.

The operator part  $\mathcal{H}_H^i(M)$  of the interaction with an alternating magnetic field having a low frequency ω and an amplitude h is odd with respect to the time reversal operation, and therefore for an ion for an even number of electrons it has for the states |ξ<sub>0</sub>⟩ and |ξ̄<sub>0</sub>⟩ only off-diagonal matrix elements of opposite sign.<sup>2</sup> In terms of the effective spin,  $\mathcal{H}_H^i(M)$  takes therefore the form

$$\mathcal{H}_H^i(M) = g_i \beta h_i \sum_j S_j^i \cos \omega t. \quad (5)$$

The operator  $\mathcal{H}_H^i(\text{US})$  of the interaction with the ultrasound field due to modulation of the crystal potential is even with respect to time reversal and has off-diagonal elements between |ξ<sub>0</sub>⟩ and |ξ̄<sub>0</sub>⟩, while its diagonal matrix elements for these states are equal to one another.<sup>2</sup> It can therefore be written in the form

$$\mathcal{H}_H^i(\text{US}) = \sum_j (G_+ S_j^i + G_- S_j^i) \varepsilon_0 \cos(\Omega t - \mathbf{k} \cdot \mathbf{r}_j), \quad (6)$$

where j is the index of the ion, ε<sub>0</sub> is the amplitude of the deformation, Ω is the frequency, k is the wave vector, and G is the spin-phonon interaction constant.

Since we are dealing with energy absorption from low-frequency fields, the primary absorption mechanism should be taken to be relaxation. In addition, direct transitions between the intersecting energy levels of the non-Kramers ions are also possible. Consider any two states, |α⟩ and |-α⟩, coupled by a spin-lattice transition. Their contribution to the total relaxation absorption of the energy of an alternating magnetic field is proportional to

$$|\langle \pm \alpha | \mathcal{H}_H(M) | \pm \alpha \rangle|^2 \omega \tau_{\alpha-\alpha} / (\omega^2 \tau_{\alpha-\alpha}^2 + 1), \quad (7)$$

and the corresponding contribution to the ultrasound absorption is proportional to

$$|\langle \pm \alpha | \mathcal{H}_H(\text{US}) | \pm \alpha \rangle|^2 \Omega \tau_{\alpha-\alpha} / (\Omega^2 \tau_{\alpha-\alpha}^2 + 1). \quad (8)$$

Here  $\mathcal{H}_H^i(M)$  and  $\mathcal{H}_H^i(\text{US})$  are the operator parts of (5) and (6) respectively.

Consider, by way of example, the contribution made to the absorption by intersecting levels (α = 1) corresponding to states with identical projection of the nuclear spin m<sub>I</sub>. Far from the intersection points, the mean value of the operator S<sub>x</sub> in (5) is ½ and -½ in the states |α⟩ and |-α⟩ respectively. Owing to the presence of the term ΔS<sub>x</sub> + Δ<sub>s</sub>S<sub>x</sub> in (2), the states |α⟩ and |-α⟩ at the intersection points are greatly altered and are given by

$$|\pm \alpha \rangle = 2^{-1/2} (|1/2 \rangle \pm |-1/2 \rangle) |m_I \rangle,$$

and the mean value of the operator S<sub>x</sub> in either state becomes equal to zero. As seen from (7), the contribution of this pair of levels to the relaxation absorption vanishes in this case.

As for the absorption due to transitions in the spectrum of the paramagnetic ion, it occurs on the contrary, only near the intersection points, since we are dealing here with absorption of low-frequency quanta. If it is assumed that on the whole the relaxation contribution predominates at T = 4.2 K, then it is clear that the alternating magnetic field absorption curve will have a local minimum at the intersection point. Furthermore, since ω, Ω ~ 2π · 10<sup>7</sup> sec<sup>-1</sup>, one can expect satisfaction of the conditions ωτ<sub>α-α</sub>, Ωτ<sub>α-α</sub> ≫ 1, even though the ions with even numbers of electrons are strongly coupled to the lattice vibrations. The Debye functions in (7) and (8) can therefore be replaced respectively by (ωτ<sub>α-α</sub>)<sup>-1</sup> and (Ωτ<sub>α-α</sub>)<sup>-1</sup>. Since the direct spin-lattice coupling of the intersecting levels is effected by low-frequency phonon modes corresponding to a low spectral density of the phonons, it follows that the Orbach-Aminov relaxation process is more effective for such states. In this case, however, the relaxation absorption should decrease with temperature like exp(-δ/k<sub>B</sub>T) and one can expect direct absorption to begin to predominate quite rapidly with decreasing temperature. This agrees with the experimentally observed replacement of the "emission" line by an absorption line when the temperature is lowered.

As for ultrasound absorption, in contrast to the mean value of the operator S<sub>x</sub>, the mean value of the operator S<sub>x</sub> differs from zero only near the intersection points. Therefore the ultrasound relaxational absorption, just as the direct absorption, is concentrated near the intersection points. It is not surprising that no ultrasound "emission" line has been observed.

Other features of the absorption can also be explained by taking joint accounts of the contributions of the relaxational and direct absorptions. A qualitative discussion of these features, similar to that presented above, would take up too much space; we proceed therefore to the quantitative theory, in the course of which the necessary clarifications will be made.

Using projection operators, the Hamiltonian (2) can be rewritten in the form

$$\mathcal{H}_\alpha = \sum_{\alpha=-8}^{\alpha=8} E_\alpha P_{\alpha\alpha}. \quad (9)$$

In fields corresponding to  $2g_{\parallel}\beta H_z/A_{\parallel} = 1, 3, 5, 7$ , the energies and eigenfunctions with  $-3 \leq \alpha \leq 3$  can be approximately obtained from the solution of the secular equations. For example:

$$\begin{aligned} E_1 &= [\varepsilon^2 + \Delta^2]^{1/2}, & |1\rangle &= A_1 |^1/2, m_1\rangle + B_1 |^{-1/2}, m_1\rangle, \\ E_{-1} &= -E_1, & |-1\rangle &= B_1 |^1/2, m_1\rangle - A_1 |^{-1/2}, m_1\rangle, \\ E_2 &= (A_{\parallel} - [\varepsilon^2 + B^2 \kappa^2]^{1/2})/2, & |2\rangle &= A_2 |^1/2, m_1-1\rangle - B_2 |^{-1/2}, m_1+1\rangle, \\ E_3 &= (A_{\parallel} + [\varepsilon^2 + B^2 \kappa^2]^{1/2})/2, & |3\rangle &= B_2 |^1/2, m_1-1\rangle + A_2 |^{-1/2}, m_1+1\rangle, \end{aligned} \quad (10)$$

where

$$\begin{aligned} \varepsilon &= g_{\parallel}\beta H_z + A_{\parallel} m_1, & \kappa &= 2[I^2(I+1)^2 - 2I(I+1)m_1^2 + m_1^2(m_1^2-4)]^{1/2}, \\ A_1 &= (\Delta_x + i\Delta_y)/C_1, & B_1 &= (\varepsilon - 2E_1)/C_1, & C_1 &= [\Delta^2 + (\varepsilon - 2E_1)^2]^{1/2}, \\ A_2 &= (\varepsilon + A_{\parallel} - 2E_3)/C_2, & B_2 &= B\kappa/C_2, & C_2 &= [B^2\kappa^2 + (\varepsilon + A_{\parallel} - 2E_3)^2]^{1/2}. \end{aligned}$$

States with  $\alpha = -2$  and  $-3$  can be obtained similarly. The remaining states are the same as those far from the intersection points.

In fields corresponding to  $2g_{\parallel}\beta H/A_{\parallel} = 0, 2, 4$ , and  $6$  the expressions for  $E_\alpha$  and  $|\alpha\rangle$  ( $-2 \leq \alpha \leq 2$ ) are

$$\begin{aligned} E_2 &= (A_{\parallel}/2 + [\varepsilon^2 + A_{\perp}^2 \lambda^2]^{1/2})/2, & |2\rangle &= A_3 |^1/2, m_1-1\rangle + B_3 |^{-1/2}, m_1\rangle, \\ E_1 &= (A_{\parallel}/2 - [\varepsilon^2 + A_{\perp}^2 \lambda^2]^{1/2})/2, & |1\rangle &= B_3 |^1/2, m_1-1\rangle - A_3 |^{-1/2}, m_1\rangle, \end{aligned} \quad (11)$$

where

$$\begin{aligned} \lambda &= 2[I(I+1) - m_1(m_1-1)]^{1/2}, & A_3 &= A_{\perp}\lambda/C_3, \\ B_3 &= (\varepsilon + A_{\parallel}/2 - 2E_2)/C_3, & C_3 &= [A_{\perp}^2\lambda^2 + (\varepsilon + A_{\parallel}/2 - 2E_2)^2]^{1/2}. \end{aligned}$$

The states with  $\alpha = -1$  and  $-2$  can be obtained in exactly the same way. The remaining states remain likewise unchanged. The values of  $m_1$  at the intersection points  $0, 2, 4$ , and  $6$  correspond to that point of intersection of levels with the same values of  $m_1$  which is to the right of the considered field value.

We now express the operators (5) and (6) in terms of the projection operators. Near the points  $1, 3, 5$ , and  $7$ :

$$\begin{aligned} \mathcal{H}_H^i(M) &= \frac{1}{2} g_{\parallel}\beta h_1^2 \cos \omega t \sum_j \left\{ [\varepsilon(P_{11}^j - P_{-1-1}^j) + (\Delta_x + i\Delta_y) P_{1-1}^j \right. \\ &\quad \left. + (\Delta_x - i\Delta_y) P_{-11}^j] (\varepsilon^2 + \Delta^2)^{-1/2} + [\varepsilon(P_{33}^j - P_{22}^j + P_{-2-2}^j - P_{-3-3}^j) \right. \\ &\quad \left. + B\kappa(P_{32}^j + P_{23}^j + P_{-3-2}^j + P_{-2-3}^j)] (\varepsilon^2 + B^2\kappa^2)^{-1/2} + \sum_{n \in \{-3, 3\}} (P_{nn}^j - P_{-n-n}^j) \right\} \end{aligned} \quad (12)$$

$$\begin{aligned} \mathcal{H}_H^i(\text{US}) &= -\frac{1}{2} \sum_j \{ [(\Delta_x + i\Delta_y) G_- + (\Delta_x - i\Delta_y) G_+] (P_{11}^j - P_{-1-1}^j) \\ &\quad \times (\varepsilon^2 + \Delta^2)^{-1/2} + [(\varepsilon - [\varepsilon^2 + \Delta^2]^{1/2})^2 G_- - (\Delta_x - i\Delta_y)^2 G_+] [(\varepsilon - [\varepsilon^2 + \Delta^2]^{1/2}) \\ &\quad + \Delta^2]^{-1} P_{-11}^j + \text{H.c.} \} \varepsilon_0 \cos(\Omega t - \mathbf{k}\mathbf{r}_j). \end{aligned} \quad (13)$$

Near the points  $0, 2, 4$ , and  $6$

$$\begin{aligned} \mathcal{H}_H^i(M) &= \frac{1}{2} g_{\parallel}\beta h_1^2 \cos \omega t \sum_j \left\{ [\varepsilon(P_{22}^j - P_{11}^j + P_{-1-1}^j - P_{-2-2}^j) \right. \\ &\quad \left. + A_{\perp}\lambda(P_{21}^j + P_{12}^j + P_{-1-2}^j + P_{-2-1}^j)] (\varepsilon^2 + A_{\perp}^2\lambda^2)^{-1/2} + \sum_{n \in \{-2, 2\}} (P_{nn}^j - P_{-n-n}^j) \right\}. \end{aligned} \quad (14)$$

There is no interaction with the sound in the vicinity of these points. The operators contain projection operators that are diagonal in the indices and are responsible for the relaxation absorption, as well as off-diagonal operators that cause direct transitions in the ion energy spectrum.

The absorption of the energy of low frequency fields, regarded as the linear response of the system to a weak perturbation, can be connected with the im-

aginary part of the generalized susceptibility<sup>8</sup>:

$$\overline{dE}/dt = \omega [\chi_r''(M) + \chi_d''(M)]/2 + \Omega [\chi_r''(\text{US}) + \chi_d''(\text{US})]/2.$$

The susceptibility components  $\chi_r''$  are due to relaxation absorption, while  $\chi_d''$  are due to direct transitions in the spectrum of the paramagnetic ions under the influence of the low-frequency fields. Using the Callen-Welton relations,<sup>8</sup> we can relate the quantities  $\chi''$  with the corresponding correlation functions of the operators  $P_{\alpha\beta}^j$ . Assuming that  $\Delta_x$  and  $\Delta_y$  have independent Gaussian distributions about zero, and in the simplest manner with the aid of the distribution function  $f(\varepsilon') = \gamma / \{\pi[(\varepsilon - \varepsilon')^2 + \gamma^2]\}$ , taking the dipole fields into account, we obtain at the points  $1, 3, 5$ , and  $7$

$$\begin{aligned} \chi_r''(M) &= D_1 \left\{ \int_0^{\infty} d(\Delta^2) \int_{-\infty}^{\infty} d\varepsilon' P(\Delta^2) f(\varepsilon') [(\varepsilon')^2 K_{1-1}(\omega) [(\varepsilon')^2 + \Delta^2]^{-1} \right. \\ &\quad \left. + (\varepsilon')^2 (K_{32}(\omega) + K_{-2-3}(\omega)) [(\varepsilon')^2 + B^2\kappa^2]^{-1} + \sum_{n \in \{1-3, 3\}} K_{n-n}(\omega) \right\}, \end{aligned} \quad (15)$$

$$\begin{aligned} \chi_d''(M) &= D_1 \left\{ \int_0^{\infty} d(\Delta^2) \int_{-\infty}^{\infty} d\varepsilon' P(\Delta^2) f(\varepsilon') [\Delta^2 \Phi_{1-1}(\omega) [(\varepsilon')^2 + \Delta^2]^{-1} \right. \\ &\quad \left. + B^2\kappa^2 (\Phi_{32}(\omega) + \Phi_{-3-2}(\omega)) [(\varepsilon')^2 + B^2\kappa^2]^{-1} \right\}, \end{aligned} \quad (16)$$

$$\chi_r''(\text{US}) = D_2 \int_0^{\infty} d(\Delta^2) \int_{-\infty}^{\infty} d\varepsilon' P(\Delta^2) f(\varepsilon') [\Delta^2 K_{1-1}(\Omega) [(\varepsilon')^2 + \Delta^2]^{-1}], \quad (18)$$

$$\chi_d''(\text{US}) = D_2 \int_0^{\infty} d(\Delta^2) \int_{-\infty}^{\infty} d\varepsilon' P(\Delta^2) f(\varepsilon') [1 + (\varepsilon')^2 / [(\varepsilon')^2 + \Delta^2]] \Phi_{1-1}(\Omega),$$

where

$$\begin{aligned} P(\Delta^2) &= \Delta_0^{-2} \exp(-\Delta^2/\Delta_0^2), & D_1 &= N\pi\omega (g_{\parallel}\beta h_1^2)^2 (16k_B T)^{-1}, \\ & & D_2 &= N\pi\Omega (|G|e_0)^2 (16k_B T)^{-1}, \end{aligned}$$

$N$  is the number of ions in the sample, and the correlators

$$\begin{aligned} K_{\alpha\beta}(\omega) &= (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle [P_{\alpha\alpha}(t) - P_{\beta\beta}(t)] [P_{\alpha\alpha} - P_{\beta\beta}] \rangle_0 / \langle (P_{\alpha\alpha} - P_{\beta\beta})^2 \rangle_0; \\ \Phi_{\alpha\beta}(\omega) &= (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle P_{\alpha\beta}(t) P_{\beta\alpha} \rangle_0 / \langle P_{\alpha\beta} P_{\beta\alpha} \rangle_0 \end{aligned}$$

are approximately written in the form

$$K_{\alpha\beta}(\omega) = [\pi\tau_{\alpha\beta}(\omega^2 + \tau_{\alpha\beta}^{-2})]^{-1},$$

where  $\tau_{\alpha\beta}^{-1}$  is the rate of the relaxation transition between the states and  $|\alpha\rangle$  and  $|\beta\rangle$ , and

$$\Phi_{\alpha\beta}(\omega) = \delta(E_\alpha - E_\beta - \hbar\omega). \quad (19)$$

We assume that  $\Delta_0 > \gamma$ ;  $\hbar\Omega \ll \Delta_0$ ,  $\gamma(\Delta_0 \approx 0.03 \text{ cm}^{-1} \approx 50 \text{ Oe})$ ; an estimate of  $\gamma$  using the equations of the statistical theory,<sup>9</sup> recognizing that  $g_{\perp} = 0$  at an  $\text{Ho}^{3+}$  ion density  $c \approx 0.005$ , yields  $\gamma \approx 0.01 \text{ cm}^{-1} \approx 16 \text{ Oe}$ ;  $\hbar\omega$ ,  $\hbar\Omega \approx 3 \cdot 10^{-4} \text{ cm}^{-1} \approx 0.5 \text{ Oe}$ . It is also natural to assume that at helium temperatures the spin-lattice coupling of states that differ in energy ( $E_\alpha - E_\beta \sim g_{\parallel}\beta H$ ,  $A_{\parallel}$ ), is via direct processes. As for the quasidegenerate states at the level intersection points, direct processes, as already mentioned, are not very likely to be effective because of the low density of the lattice oscillators:  $\rho_{\text{ph}} \sim (E_\alpha - E_\beta)^2$ . It can be assumed that these states are coupled by Ohrbach relaxation:  $\tau_{\alpha\beta}^{-1} \sim \exp(-\delta/k_B T)$  (Ref. 10). It is easy to show that  $\tau_{\alpha\beta}^{-1}$  for states con-

taining wave functions with different values of  $m_l$  is given by

$$\begin{aligned} \tau_{\alpha\beta}^{-1}(\varepsilon) &= B^2 \kappa^2 \tau^{-1}(0) (\varepsilon^2 + B^2 \kappa^2)^{-1} \quad (\Delta m_l = 2), \\ \tau_{\alpha\beta}^{-1}(\varepsilon) &= A_{\perp}^2 \lambda^2 \tau^{-1}(0) (\varepsilon^2 + A_{\perp}^2 \lambda^2)^{-1} \quad (\Delta m_l = 1). \end{aligned}$$

The relation  $\tau_{\alpha\beta}^{-1}(\varepsilon) \approx \tau^{-1}(0)$  is of no significance for intersecting states with  $\Delta m_l = 0$ . In addition,  $\tau_{\alpha\beta}^{-1} = \tau_{\beta-\alpha}^{-1}$ . Taking all the foregoing into account, as well as the earlier assumptions  $\omega \tau_{\alpha-\alpha}, \Omega \tau_{\alpha-\alpha} \gg 1$ , we present a few estimates. At the points 1, 3, 5, and 7

$$\chi_r''(M) \approx F_1 T^{-1} \left\{ (\omega \tau(0))^{-1} \left[ (\varepsilon^2 / \Delta_0^2) \exp(\varepsilon^2 / \Delta_0^2) E_1(\varepsilon^2 / \Delta_0^2) + 2 \int_{-\infty}^{\infty} (\varepsilon')^2 B^2 \kappa^2 f(\varepsilon') / (\varepsilon'^2 + B^2 \kappa^2)^2 d\varepsilon' \right] + \sum_{\alpha \neq [-3, 3]} (\omega \tau_{\alpha-\alpha})^{-1} \right\}; \quad (20)$$

$$\chi_d''(M) \approx F_1 T^{-1} \left\{ 5(\hbar \omega)^2 \gamma \Delta_0^{-2} (\varepsilon^2 + \gamma^2)^{-1} + 4 B^2 \kappa^2 \gamma (\varepsilon^2 + \gamma^2)^{-1} (\hbar^2 \omega^2 - B^2 \kappa^2)^{-1/2} \right\}; \quad (21)$$

if  $B^2 \kappa^2 < \hbar^2 \omega^2$ . In the opposite case the second term of (21) vanishes identically. The terms containing  $B \kappa$  vanish identically also at the point 7. The divergence in the denominator of the second term in (21) is due to the use of the function (19). We note that the function  $\Phi_{\alpha\beta}(\omega)$  has a finite width all the same, owing to the flip-flop processes between the intersecting levels:

$$\begin{aligned} \chi_r''(\text{US}) &\approx F_2 T^{-1} [\Omega \tau(0)]^{-1} \left\{ 1 - (\varepsilon^2 / \Delta_0^2) \exp(\varepsilon^2 / \Delta_0^2) E_1(\varepsilon^2 / \Delta_0^2) \right\}, \quad (22) \\ \chi_d''(\text{V3}) &\approx F_2 T^{-1} (\hbar \Omega)^2 \gamma (\varepsilon^2 + \gamma^2)^{-1} \Delta_0^{-2}. \end{aligned}$$

Here  $F_1 = N(g_{\parallel} \beta \hbar^2)^2 / (16 k_B)$ ,  $F_2 = N(|G| \varepsilon_0)^2 / (16 k_B)$ . (23)

Expressions for  $\chi''$  in the vicinities of the points 0, 2, 4, and 6 were obtained in similar fashion:

$$\begin{aligned} \chi_r''(M) &\approx F_1 T^{-1} \left\{ 2(\omega \tau(0))^{-1} \int_{-\infty}^{\infty} A_{\perp}^2 \lambda^2 (\varepsilon')^2 f(\varepsilon') / (\varepsilon'^2 + A_{\perp}^2 \lambda^2)^2 d\varepsilon' + \sum_{\alpha \neq [-2, 2]} (\omega \tau_{\alpha-\alpha})^{-1} \right\}, \quad (24) \\ \chi_d''(M) &\approx F_1 T^{-1} A_{\perp}^2 \lambda^2 \gamma (\varepsilon^2 + \gamma^2)^{-1} (\hbar^2 \omega^2 - A_{\perp}^2 \lambda^2)^{-1/2}, \quad (25) \end{aligned}$$

if  $\hbar^2 \omega^2 > A_{\perp}^2 \lambda^2$ . In the opposite case  $\chi_d''(M) = 0$ . The values of  $\chi_r''(\text{US})$  and  $\chi_d''(\text{US})$  are identically zero. The function  $E_1(x)$ , which is a modification of the integral exponential function, is tabulated in Ref. 11.

The quantity  $(\varepsilon^2 / \Delta_0^2) \exp(\varepsilon^2 / \Delta_0^2) E_1(\varepsilon^2 / \Delta_0^2)$  tends to zero at  $(\varepsilon^2 / \Delta_0^2) \ll 1$  and to unity at  $(\varepsilon^2 / \Delta_0^2) \gg 1$  and its half width at half maximum is  $\sim \Delta_0$ . We have

$$\begin{aligned} &\int_{-\infty}^{\infty} A_{\perp}^2 \lambda^2 (\varepsilon')^2 f(\varepsilon') / (\varepsilon'^2 + A_{\perp}^2 \lambda^2)^2 d\varepsilon' \\ &\approx \begin{cases} \varepsilon^2 A_{\perp}^2 \lambda^2 / (\varepsilon^2 + A_{\perp}^2 \lambda^2)^2 & \text{if } A_{\perp}^2 \lambda^2 \gg \gamma^2, \\ \pi^{-1} A_{\perp} \lambda \gamma / (\varepsilon^2 + \gamma^2) & \text{if } A_{\perp}^2 \lambda^2 \ll \gamma^2. \end{cases} \end{aligned} \quad (26) \quad (27)$$

The physical meaning of these approximations is easily understood. If the scatter of the local magnetic fields is relatively small ( $A_{\perp}^2 \lambda^2 \gg \gamma^2$ ) the energy levels of practically all ions intersect at a definite value of the external magnetic field  $H$ , corresponding to  $\varepsilon = 0$ , and there is no relaxation absorption in this field: the function (26) has a local minimum at  $\varepsilon = 0$ . If, however, the scatter is large ( $A_{\perp}^2 \lambda^2 \ll \gamma^2$ ), only a small fraction of the ions for which the local field is zero does not contribute to the relaxation absorption; the absorption at  $\varepsilon = 0$  is therefore different from zero, a fact reflected in the estimate (27).

The same can be stated concerning the integral in (20), where  $A_{\perp} \lambda$  is replaced by  $B \kappa$ .

## 5. DISCUSSION OF RESULTS

The parameter  $B$  was calculated from Eq. (4) using the wave functions of the lower doublet and of the first excited singlet, obtained by I. N. Kurkin and E. A. Tsvetkov on the basis of the data of Ref. 3:

$$\begin{aligned} |\xi_0\rangle, |\xi_1\rangle &= 0.8136 | \pm 7 \rangle - 0.5766 | \pm 3 \rangle + 0.0568 | \mp 1 \rangle - 0.0489 | \mp 5 \rangle, \\ |\xi_2\rangle &= 0.6069 | \pm 6 \rangle - 0.3629 | \pm 2 \rangle + 0.3629 | -2 \rangle - 0.6069 | -6 \rangle \end{aligned}$$

and amounted to  $B \approx 0.002 \text{ cm}^{-1} \approx 3.13 \text{ Oe}$ .

Since we do not know the form of the Hamiltonian  $\Delta \mathcal{H}_{\text{cr}}(J)$ , the value of the parameter  $A_{\perp}$  at  $H \parallel z$  was estimated from the formula  $A_{\perp} \sim \Delta_0 A / \delta \approx 9 \cdot 10^{-5} \text{ cm}^{-1} \approx 0.14 \text{ Oe}$ . We have  $\kappa \approx 31.0, 26.8, 18.4$ , and 0 at the points 1, 3, 5, and 7, respectively and  $\lambda \approx 7.6, 7.0$ , and 5.2 at the points 2, 4, and 6. Since  $B \kappa > \gamma$  at points 1, 3, 5 and  $A_{\perp} \lambda < \gamma$ , the integrals in (20) and (24) were replaced respectively by the approximate expressions (26) and (27) [ $A_{\perp} \lambda$  in (26) must be replaced by  $B \kappa$ ]. The second term in (21) was excluded, since  $\hbar \omega < B \kappa$ . According to our estimates  $A_{\perp} \lambda > \hbar \omega$ , but  $A_{\perp}$ , as well as  $\Delta$ , has no definite value and is distributed near  $A_{\perp} = 0$  at  $H \parallel z$ . Therefore those ions for which  $A_{\perp} \lambda < \hbar \omega$  contribute to direct absorption of the energy of the alternating magnetic field at the points 0, 2, 4, and 6.

Far from the intersection points, only

$$\chi_r''(M) = (g_{\parallel} \beta \hbar^2)^2 (16 k_B T)^{-1} \sum_{\alpha} (\omega \tau_{\alpha-\alpha})^{-1}$$

differs from zero. Since the energy distances ( $E_{\alpha} - E_{-\alpha}$ ) increase on the whole with increasing field, the rates of the direct spin-lattice relaxation processes also increase. Accordingly, the absorption as a whole increases. Local singularities occur at the intersection points. At points 1, 3, 5, and 7 there is a local minimum of  $\chi_r''(M)$  and a maximum of  $\chi_d''(M)$ . If at some temperature  $\chi_r''(M) + \chi_d''(M)$  has on the whole a local minimum, this minimum should be replaced by a maximum with decreasing temperature, since  $\chi_r''(M) \sim \exp(-\delta/k_B T)$ . The temperature dependence of the local extremum of  $\chi_r''(M) + \chi_d''(M)$  at the points 1, 3, 5, 7 made it possible to separate the term corresponding to  $\chi_r''(M)$ . Its contribution to  $\chi_r''(M) + \chi_d''(M)$  is  $\sim 80\%$  at 4.2 K. From the dependence of this contribution on the temperature (Fig. 3) it was possible to determine  $\delta \approx 9.8 \pm 1 \text{ cm}^{-1}$ , which agrees with the value  $\delta \approx 9 \text{ cm}^{-1}$  obtained earlier by spectroscopic methods.<sup>3</sup>

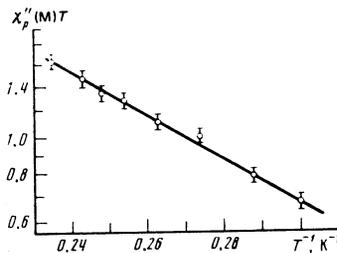


FIG. 3. Plot of  $\chi_r''(M)T$  at the point corresponding to  $2g_{\parallel} \beta H_z A_{\perp} = 5$  vs temperature.

Figure 1c shows the derivative of the spectrum at 4.2 K, obtained from Eqs. (20), (21), (24), and (25) with allowance for (26) and (27), using the parameters  $\gamma$  and  $\Delta_0$  cited above (no account was taken of direct relaxation processes, which cause a monotonic increase of the absorption with increasing field). A consequence, which in our opinion is subject to no doubt, with the experimental data is obtained at  $B \approx 1$  Oe. At the value of  $B$  estimated from Eq. (4), the lines at the points 1, 3, and 5 are found to be somewhat wider than those observed in experiment.

With increasing angle  $\theta$  between  $H$  and the  $C_4$  axis of the crystal, i.e., when a transverse magnetic-field component  $H_1$  appears, the quantity

$$A_1 \lambda \sim g_1 \beta H_1 A \langle \xi_x | J_x | \xi_x \rangle / 2\delta$$

increases and can exceed  $\gamma$ . The integral in (24) will then have to be replaced not by the function (27), which has a maximum at the points 0, 2, 4, and 6, but by the function (26), which has a local minimum at these points. This is indeed observed in experiment: the absorption maximum goes over smoothly into a minimum when the angle  $\theta$  is increased (Fig. 2).

Using the experimentally obtained relative values of  $\chi''(M)$  and  $\chi_4''(M)$  at points 1, 3, and 5 we can estimate the parameter  $\tau(0)$ . In our case it was found to be  $\tau(0) \sim 10^{-4}$  sec at 4.2 K, which is perfectly reasonable. We note that the absorption due to direct processes, which depends monotonically on the field, exceeds by more than an order of magnitude the absorption due to Orbach relaxation processes, i.e., for the direct processes we have  $\tau < 0.1\tau(0)$ , and the value  $\tau < 10^{-5}$  sec cited in Ref. 12 for  $\text{Ho}^{3+}$  in  $\text{CaWO}_4$  at 1.5 K corresponds more readily to just these processes.

At a temperature lower than 2 K the relaxation absorption due to Orbach-Aminov processes vanishes and what is left are the absorption due to direct transitions between the levels near the intersection point, and the absorption due to direct relaxation processes. We note that the spectrum of the direct absorption of energy from a low-frequency alternating magnetic field parallel to the  $z$  axis was observed before<sup>13</sup> in single-crystal  $\text{LaES:Ho}^{3+}$ .

The ultrasound absorption coefficient  $\sigma$  (Ref. 10) can be connected with  $\chi''(\text{US})$  by the relation

$$\sigma(\Omega) = \Omega \chi''(\text{US}) / \rho v_l^2 \epsilon_0^2 V, \quad (28)$$

where the crystal density  $\rho \approx 6.15$  g/cm<sup>3</sup>,  $v_l$  is the speed of sound in the crystal, and  $N/V \approx 6.4 \times 10^{19}$  cm<sup>-3</sup> is the number of paramagnetic particles per unit volume. Comparing the experimentally measured value of  $\sigma$  with the one calculated from (28), we found that the constant  $|G|$  of the spin-phonon coupling due to the direct modulation of the crystal field by the acoustic wave should be of the order of  $10^3$  cm<sup>-1</sup>. In principle, non-Kramers ions actually have a strong spin-phonon coupling. In particular, theoretical estimates for a sound wave propagating perpendicular to the trigonal axis in ethyl sulfate containing  $\text{Ho}^{3+}$  ions lead to a value  $|G| \sim 10^3$  to  $10^4$  cm<sup>-1</sup> (Ref. 10). It follows from symmetry considerations, however, that sound propagating

along the  $z$  axis of an undistorted complex of symmetry  $S_4$  cannot be absorbed by  $\text{Ho}^{3+}$  ions. Allowance for the local distortions of the symmetry lifts the hindrance, but leads to an additional small factor  $\sim \Delta_0/\delta$ . A reasonable estimate in our case is therefore  $|G| \sim 1$  to  $10$  cm<sup>-1</sup>. It is also difficult to understand why the sound-absorption line width differs somewhat from that of the absorption of an alternating magnetic field at point 7. This raises the question of the real character of the spin-phonon coupling of the  $\text{Ho}^{3+}$  ions in  $\text{CaWO}_4$ , and possibly of its operator structure, which can differ from (6). These discrepancies between theory and experiment call for a special analysis.

We note in conclusion that the method of nonresonant paramagnetic absorption turned out in our case to be very convenient and very informative. The convenience was that the specific character of the energy spectrum of the  $\text{Ho}^{3+}$  ion makes the absorption signals resonant with the field, so that it becomes very easy to record them. This has made it possible, first, to obtain purely spectroscopic information, which is difficult and sometimes impossible to obtain by the ESR method, namely the small values of the constants  $A_1$  and  $B$  in the spin Hamiltonian, and the spread of the local fields  $\gamma$ ; second, to confirm the correctness of the values of  $\Delta_0$  and  $\delta$  obtained by spectroscopic methods; third, to obtain for the relaxation times and mechanisms traditional data that cannot be obtained in our case by the method of pulsed saturation of the ESR lines.<sup>12</sup> We note also that study of the absorption of low-frequency sound can yield in principle information on the spin-phonon coupling cross section.

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