Relaxational paramagnetic sound absorption under conditions of a dipole-dipole-interaction temperature shift

A. V. Duglav, N. G. Koloskova, B. I. Kochelaev, and A. Kh. Khasanov

Kazan' State University

(Submitted 16 June 1980)
Zh. Eksp. Teor. Fiz. **79**, 2367–2373 (December 1980)

Results are reported of an investigation of the cross-relaxation absorption of 20 MHz sound by Cr^{3+} in ruby at 4.2 K, due to a stationary shift of the temperature T_{dd} of their dipole-dipole interaction pool (DDP). Experiment has shown that the acoustic absorption is uniquely determined by the value of the T_{dd} shift and reaches $\sim 10^{-7}$ cm^{-1} at $T_{dd} \approx 0.21$ K. It is shown theoretically that the effect is du effect is due to direct sound-induced transitions between the DDP levels. These transitions are allowed in the case when the single-particle spin energy-level spacings are equal. It is noted that the use of nonequilibrium DDP states extends the experimental capabilities of the techniques of relaxation paramagnetic sound absorption.

PACS numbers: 62.65. + k, 43.35.Fj, 43.35.Sx, 75.20.En

1. INTRODUCTION

It is known that relaxation paramagnetic sound absorption[1] is the analog of nonresonant paramagnetic absorption of the energy of an alternating magnetic field, also known as absorption in parallel fields. Just as in the case of acoustic paramagnetic resonance (APR),[2] the study of relaxation absorption of sound yields direct information on the dynamic characteristics of the interaction between paramagnetic centers and crystal-lattice vibrations. The resonance method encounters difficulties due to the complexity of measurements in the hypersound frequency range, and to the restrictions imposed on the number of investigated substances by the stringent requirements with respect to their mechanical and chemical properties (the latter is corroborated by the fact that almost no APR studies of water-soluble paramagnetic crystals have been made so far).

Measurements of relaxation sound absorption, which can be performed at lower frequencies $\sim 10^5 - 10^8$ Hz, are much less affected by these restrictions. The reason for the small number of experiments performed by this method (see, e.g., Ref. 3) is apparently that for most transition-group ions the relaxation-absorption effect is weak and does not exceed $\sim 10^{-6}$ cm^{-1} even in substances with maximum possible paramagnetic-center density. It is therefore difficult to separate this effect from the sound absorption due to factors not connected with the magnetic properties of the samples.

Atsarkin and Ryabushkin[4] have shown that the nonequilibrium states of the dipole-dipole pool (DDP) of the interactions of the paramagnetic centers, states resulting from not strictly resonantly saturated EPR, can increase the absorption in parallel fields by many times. Following the aforementioned analogy, one can expect a strong shift of the DDP temperature to cause an equally appreciable increase in the relaxation absorption of sound. To check on this idea, observations were made of the nonequilibrium cross-relaxation absorption of sound by Cr^{3+} ions in ruby, and the preliminary results are briefly reported in Ref. 5. This experiment is described in the present article in greater detail and the corresponding theory of the phenomenon is presented.

2. EXPERIMENTAL PROCEDURE AND RESULTS

The experiment was performed on a ruby crystal with approximate Cr^{3+} ion density 0.05 at.% at 4.2 K. From among the many cross-relaxation situations in ruby, which differ in the strength of the constant magnetic field and in the angle between the C_3 axis of the crystal and the magnetic field, we chose a situation wherein the cross-relaxation absorption of the alternating magnetic field energy is most strongly pronounced.[6] At an external magnetic field $H_{cr} \approx 1320$ Oe and at an angle $\theta \approx 26°$ between the C_3 axis and the magnetic field, cross relaxation affects the energy levels 2, 3, and 4 of the Cr^{3+} ions ($\nu_{23} = \nu_{34} \approx 4.7$ GHz, the levels are numbered in order of increasing energy). In addition, the resonance frequency of the 2–4 transition in this field is situated in the 3-cm band, in which it is convenient to produce a disequilibrium in the DDP (Fig. 1). Notice must be taken of the resonant character of the cross-relaxation absorption, since the frequencies of the 2–3 and 3–4 transitions are equal at a definite value of the external magnetic field.

The cross-relaxation absorption of the ultrasound was registered with an autodyne acoustic-absorption detector.[7] A sample measuring $\sim 1 \times 1 \times 0.5$ cm, so finished that the working faces were parallel within 10 in., was combined with a 20-MHz X-cut quartz piezoconverter to form an acoustic resonator. The converter was thermocompression-welded to the crystal.[8] The acoustic coupling obtained in this manner was

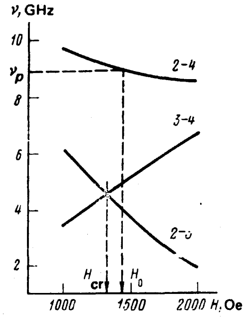

FIG. 1. EPR frequencies of the transitions 2–3, 3–4, and 2–4 of Cr^{3+} in ruby vs. the external magnetic field at $\theta = 26°$ (ν_p is the pump frequency).

0038-5646/80/121199-04$02.40

transparent to both longitudinal and transverse sound, and withstood repeated cooling to liquid-helium temperature without adverse effects.

The acoustic resonator of the autodyne was excited at one of the overtones. In the experiment, longitudinal sound of frequency 19619.8 kHz was propagated along the C_3 axis, of the crystal. At 4.2 K, the acoustic resonator had an equivalent resonant acoustic resistance $R_a = 640\ \Omega$, corresponding to a background damping $\alpha_b \approx 10^{-2}$ cm^{-1}, and a mechanical-resonance peak width $\Delta f \approx 2.7$ kHz at the 0.7 level. The measured longitudinal ultrasound velocity was $v \approx 11.24 \times 10^5$ cm/sec.

To increase the sensitivity of the acoustic-absorption spectrometer we used square-wave modulation of the magnetic field, followed by synchronous detection of the absorption signal.[9] In this modulation method it is possible to effect both differential passage through the absorption line at low modulation amplitude, and registration of the absorption line itself without distortion of its waveform at a modulation swing exceeding the line width by several times. The spectrometer sensitivity is several times higher in the latter case than in the differential-passage regime. We have realized the indicated procedure by assembling the apparatus described by Sadykov.[10] The modulation frequency was 8 Hz and the amplitude swing was up to 130 Oe in a magnet gap 75 mm.

To produce a disequilibrium of the Cr^{3+}-ion DDP, the acoustic resonator was placed in a rectangular 3-cm-band waveguide at a distance of 3/4 wavelength from the shorted end, in the antinode of the magnetic component of an H_{10} electromagnetic wave (Fig. 2). One of the piezoconverter electrodes, which was coated on the sample, was galvanically connected to the narrow wall of the waveguide and served simultaneously as the wall part that covered the opening for the piezoconverter. This measuring-cell construction prevented the electromagnetic field applied to the piezoconverter from penetrating into the sample. To observe and measure the parameters of the Cr^{3+}-ion EPR line at the 2–4 transition frequency, we used an ordinary 3-cm-band spectrometer with high-frequency modulation of the magnetic field. The modulating coil was wound directly on the sample. The same coil, together with a Pound-Knight autodyne, was used to observe the cross-relaxation absorption of the energy of the alternating magnetic field.

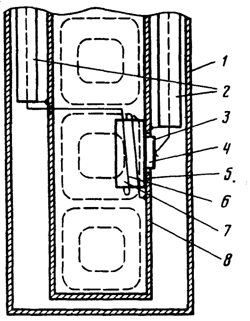

FIG. 2. Simplified diagram of measurement cell: 1–screen 2–coaxial cables, 3–silver electrode, 4–piezoconverter, 5–indium electrode that serves simultaneously as an acoustic coupler, 6–coil, 7–sample, 8–waveguide. The dashed lines show the structure of the magnetic component of an H_{10} electromagnetic wave in the waveguide.

The experimental procedure was the following. The strength of the external magnetic field and the angle between the C_3 axis of the crystal and the magnetic field were chosen such that the cross-relaxation absorption signal in the parallel field was a maximum. The "acoustic" autodyne was then used to observe the cross-relaxation absorption of ultrasound at not-strictly-resonant saturation of the EPR line. The absorption signals were registered with an automatic plotter as functions of the field H, with the magnetic-field modulated by a square wave with a swing of 30 Oe.

In the experiment, the magnitude and sign of the registered cross-relaxation sound-absorption line corresponded to the temperature acquired by the DDP when the EPR line is saturated in the vicinity of the field H_{cr}. When the microwave-field frequency is changed, i.e., when position of the center of the H_0 line corresponding to the 2–4 transition is shifted relative to the pump point H_{cr}, the amplitude $\Delta\alpha$ of the cross-relaxation ultrasound-absorption signal varies smoothly. When the EPR line was saturated on its low-frequency (weak-field, $H_{cr} < H_0$) wing, the absorption was increased relative to the equilibrium value; when the EPR line was saturated on its high-frequency (strong-field, $H_{cr} > H_0$) wing, the absorption signal reversed sign, i.e., amplification of ultrasound took place. This is understandable, for in the latter case an excess energy $h(\nu - \nu_0)$ is transferred to the DDP, causing it to become "overheated" all the way to negative temperatures (here ν_0 is the Zeeman frequency corresponding to the center of the EPR line, and ν is the pump frequency. Conversely, in the first case the missing energy is drawn from the DDP, which then becomes cooled.

We measured the dependence of $\Delta\alpha$ on the position of the saturation point relative to the center of the EPR line. To this end, we measured separately the dependence of $\Delta\alpha$ on the frequency of the saturating microwave field, as well as the similar dependence of the field H_0 corresponding to the center of the unsaturated EPR line, and of the EPR line width ΔH between the inflection points. By comparing the results, we then

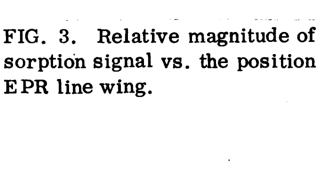

FIG. 3. Relative magnitude of cross-relaxation sound-absorption signal vs. the position of the saturation point on the EPR line wing.

plotted the curve of Fig. 3. The values of $\Delta\alpha$ of the maximal positive and negative cross-relaxation ultrasound absorption agreed within the limits of experimental error and amounted to $\Delta\alpha_{\exp} \approx (1 \pm 0.25) \times 10^{-7}$ cm^{-1}.

Since the sound absorption, which is inversely proportional to the DDP temperature, is small under equilibrium conditions, it can be reliably estimated from the absorption under nonequilibrium conditions by using the ratio of the lattice and DDP temperatures under conditions of not-strictly-resonant EPR-line saturation measured by the technique of absorption in parallel fields. The maximum temperature ratio obtained in this manner turned to be approximately twenty. Consequently, the equilibrium cross-relaxation sound absorption in this experiment was ~5×10^{-9} cm^{-1}.

3. DISCUSSION OF RESULTS

We calculate now the sound-wave absorption by a nonequilibrium spin system as a result of spin-spin interactions, for the considered case when certain intervals between the paramagnetic-center spin energy levels coincide. The Hamiltonian of such a spin system can be expressed in terms of projection operators $P^j_{\alpha\beta}$ acting in the space of single-particle wave functions.

$$P_{\alpha\beta}{}^j\psi_\gamma{}^j=\delta_{\beta\gamma}\psi_\alpha{}^j.$$

We have

$$\mathscr{H}=\mathscr{H}_0+\mathscr{H}_{\rm dd}+\mathscr{H}_{\rm in};\quad \mathscr{H}_0=\sum_{j,\alpha} E_\alpha P_{\alpha\alpha}{}^j;$$
$$\mathscr{H}_{\rm dd}=\frac{1}{2}\sum_{i,j}\sum_{\alpha,\beta,\alpha',\beta'} W^{ij}_{\alpha\beta\beta'\alpha'}P_{\alpha\beta}{}^iP^j_{\beta'\alpha'};\quad \mathscr{H}_{\rm in}=\sum_{j,\alpha}\delta_\alpha{}^jP_{\alpha\alpha}{}^j. \tag{1}$$

Here $\mathscr{H}_0$ is the spin Hamiltonian of the noninteracting paramagnetic centers; $\mathscr{H}_{\rm in}$ describes the energy-level spread that leads to inhomogeneous broadening of the EPR line; $\mathscr{H}_{\rm dd}$ is the secular part of the dipole-dipole interaction; the summation is over states whose energies satisfy the equality $E_\beta - E_\alpha = E_{\beta'} - E_{\alpha'}$. The indices i and j number the paramagnetic ions.

The interaction of the spin system with low-frequency sound (sound frequency $\hbar\omega \ll E_\beta - E_\alpha$) can be represented by the Hamiltonian

$$\mathscr{H}_s(t)=-\sum_j F_\alpha P_{\alpha\alpha}{}^j\varepsilon_0\cos(\omega t-\mathbf{q}\mathbf{r}_j)\equiv-\frac{1}{2}(\sigma_{\mathbf{q}}e^{-i\omega t}+\sigma_{-\mathbf{q}}e^{i\omega t})\varepsilon_0, \tag{2}$$

where $\varepsilon_0\cos(\omega t - \mathbf{q}\cdot\mathbf{r}_j)$ is a component of the strain tensor, $\mathbf{q}$ is the wave vector of the sound wave, and F_α is the diagonal matrix element of the spin operator. In particular, if the sound propagates along the symmetry axis Z, then $F=G[S_z^2 - S(S+1)/3]$, where G is the spin-phonon interaction constant. The off-diagonal part is omitted from (2), since the probability of a transition between different energy levels E_α under the influence of low-frequency sound is negligibly small.

We call attention above all to the circumstance that in the case of equal spacing between the single-particle spin energy levels the low-frequency sound wave causes direct transitions between the DDP energy sublevels. This is seen from the fact that the operators $\mathscr{H}_s$ and $\mathscr{H}_{\rm dd}$ do not, generally speaking, commute:

$$[\mathscr{H}_s,\mathscr{H}_{\rm dd}]=\frac{1}{2}\sum_{i,j}\sum_{\alpha,\beta,\beta',\alpha'} W^{ij}_{\alpha\beta\beta'\alpha'}[\varepsilon_i(F_\alpha-F_\beta)+(F_{\beta'}-F_{\alpha'})\varepsilon_j]P_{\alpha\beta}{}^iP^j_{\beta'\alpha'}. \tag{3}$$

On the other hand, in the case of a nonequidistant spectrum only the states $\beta' = \beta$ and $\alpha' = \alpha$ are left in the secular part of $\mathscr{H}_{\rm dd}$, and in the limit of long sound wavelength $\lambda \gg |\mathbf{r}_i - \mathbf{r}_j|$ the commutator tends to zero.

The paramagnetic absorption of sound is thus determined by the difference between the populations of the energy levels of the dipole-dipole pool, i.e., by its temperature $T_{\rm dd}$. It is convenient to express the sound-absorption coefficient $\alpha(\omega)$ in terms of the imaginary part of the acoustic susceptibility of the spin system $\chi(\omega)$, expressing it in terms of the spectral intensity $\Gamma(\omega)$ of the correlation function of the spin operators σ_q on the basis of the fluctuation-dissipation theorem:

$$\alpha(\omega)=\frac{\omega\chi''(\omega)}{\rho v^3};\quad \chi''(\omega)=\frac{2\pi}{\hbar}\operatorname{th}\frac{\hbar\omega}{2kT_{\rm dd}}\langle\sigma^2\rangle\Gamma(\omega);$$
$$\Gamma(\omega)=\frac{1}{4\pi\langle\sigma^2\rangle}\int\limits_{-\infty} e^{i\omega t}\langle\sigma(t)\sigma(0)+\sigma(0)\sigma(t)\rangle dt. \tag{4}$$

We have used here the long-wave approximation $q \to 0$; $\langle\cdots\rangle$ is a statistical mean value with a local-equilibrium density matrix.

It is natural to assume that the spectral intensity $\Gamma(\omega)$ is Lorentzian, with width $1/\tau$, and can be determined by the method of moments (see, e.g., Ref. 11):

$$\Gamma(\omega)=\frac{\tau}{\pi(1+\omega^2\tau^2)};\quad \frac{1}{\tau}=\frac{\pi}{2\sqrt{3}}\frac{M_2{}^{3/2}}{M_4{}^{1/2}M_0}. \tag{5}$$

Here M_n/M_0 are the moments of the $\Gamma(\omega)$ curve normalized to unity, and the parameter τ is in fact the resonant cross-relaxation time.

We consider now the case realized in our experiment, when the energy intervals between the levels are equal ($E_4 - E_3 = E_3 - E_2$). Direct calculations yield then

$$M_0=\langle\sigma^2\rangle=\frac{1}{4}N\sum_{\alpha=1}^{4}F_\alpha{}^2;$$
$$M_2=\langle[\sigma,\mathscr{H}_{\rm dd}]^2\rangle=\frac{1}{4}N(F_2+F_4-2F_3)^2\sum_j|W^{ij}_{2343}|^2;$$
$$M_4=\langle[[\sigma,\mathscr{H}_{\rm dd}],\mathscr{H}_{\rm dd}]^2\rangle=\frac{1}{4}N(F_2+F_4-2F_3)^2\cdot$$
$$\cdot\sum_j|W^{ij}_{2343}|^2\left[3|W_{2343}|^2+\frac{1}{2}(W_{3333}-W_{2244}-W_{2442})^2\right], \tag{6}$$

where N is the number of paramagnetic centers in the sample.

The sound-absorption coefficient takes thus the form

$$\alpha(\omega)=\frac{N_0}{2\hbar\rho v^3}\frac{\omega\tau}{1+\omega^2\tau^2}\operatorname{th}\frac{\hbar\omega}{2kT_{\rm dd}}\sum_{\alpha=1}^{4}F_\alpha{}^2 \tag{7}$$

with a parameter τ determined by formulas (5) and (6). Here N_0 is the number of paramagnetic centers per unit volume, ~2.3×10^{19} cm^{-3} in our case.

To calculate the time τ we use the concrete wave functions described in Sec. 2 for the values of the magnetic field and of its angle with the z axis. The lattice sums were estimated by averaging over the angles and by a comparison with a primitive cubic lattice in which the unit cell has the same volume for one aluminum atom in corundum. Our calculations by formulas (5) and (6) yielded $\tau \approx 0.9\times 10^{-7}$ sec.

As noted above the DDP temperature was measured by comparing the relaxation absorption of the alternating magnetic field under the same conditions as of sound, with absorption under equilibrium conditions. This yielded $T_{dd} \approx 0.21$ K. Substituting these data in (7), we obtain $\alpha_T = G^2 \cdot 0.56\times 10^{-7}$ cm^{-1}, where the constant G is in reciprocal centimeters. Comparing this result with the experimental $\Delta\alpha_{exp} \approx 10^{-7}$ cm^{-1}, we obtain the estimate $G \approx 1.3$ cm^{-1} for the spin-phonon interaction constant of the Cr^{3+} ion in ruby. This is in satisfactory agreement with results obtained by other methods ($G \approx 6$ cm^{-1}, Ref. 12), thus confirming the effectiveness of the method of relaxation paramagnetic absorption of sound under conditions of shifted DDP temperature.

[1] B. I. Kochelaev, Zh. Eksp. Teor. Fiz. **41**, 423 (1961) [Sov. Phys. JETP **14**, 305 (1962)]. N. G. Koloskova, U. Kh. Kopvillem, and B. I. Kochelaev, Fizicheskie problemy spektroskopii (Physical Problems of Spectroscopy), Vol. 2, Izd. AN SSSR, 1963, p. 91.

[2] S. A. Al'tshuler, Dokl. Akad. Nauk SSSR 85, 1235 (1952).

[3] V. A. Golenishchev-Kutuzov, Dissertation, Kazan' State Univ., 1964.

[4] V. A. Atsarkin, Zh. Eksp. Teor. Fiz. **64**, 1087 (1973) [Sov. Phys. JETP **37**, 552 (1973)]. V. A. Atsarkin and O. A. Ryabushkin, Pis'ma Zh. Eksp. Teor. Fiz. **17**, 103 (1973) [JETP Lett. **17**, 71 (1973)].

[5] S. A. Al'tshuler, A. V. Duglav, V. I. Kochelaev, and A. Kh. Khasanov, Proc. 20-th AMPERE Congress, Tallinn, 1978, p. 238.

[6] V. A. Atsarkin, Fiz. Tverd. Tela (Leningrad) **17**, 2398 (1975) [Sov. Phys. Solid State **17**, 1582 (1975)].

[7] I. I. Sadykov, Prib. Tekh. Eksp. No. 1, 129 (1978).

[8] E. K. Zittig and G. D. Cook, Trans. IEEE (Russ. transl.) **65**, No. 8, 124 (1968).

[9] E. F. Taylor and N. Bloembergen, Phys. Rev. **113**, 431 (1959).

[10] I. I. Sadykov, Prib. Tekh. Eksp. No. 6, 92 (1978).

[11] A. Abragam, Principles of Nuclear Magnetism Oxford, 1960 (Russ. transl., IIL, 1963, p. 111).

[12] E. M. Ganapol'skiĭ, and D. I. Makovetskiĭ, Fiz. Tverd. Tela (Leningrad) **15**, 2447 (1973) [Sov. Phys. Solid State **15**, 1625 (1974)]. R. B. Hemphill, P. L. Donoho, and E. D. Donald, Phys. Rev. **146**, 329 (1966).

Translated by J. G. Adashko