Spin-lattice relaxation due to flexural vibrations in layered crystals

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Spin-lattice relaxation in layered crystals is investigated theoretically and experimentally. It is shown that the presence of a flexural mode of acoustic vibrations in such crystals leads to an anomalous temperature dependence of the relaxation time in the region of the Raman processes. In particular the contribution of flexural vibrations at temperatures $\zeta\Theta < T < \Theta$ (Θ is the ratio of interlayer and intralayer elastic moduli) should result in a relation $T_1 \sim T^{-3}$ as against the $T_1 \sim T^{-7}$ characteristic of the usual case. Spin-lattice relaxation of EPR of Mn^{2+} in $CdBr_2$ and spin-lattice relaxation of quadrupole NMR of the halide nuclei in $CdBr_2$, CdI_2 and PbI_2 crystals are investigated experimentally. In all cases a region is observed in which the temperature dependence $T_1 \sim T^{-3}$ is valid, and this indicates that flexural vibrations play the main role in spin-lattice relaxation of layered crystals.

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INTRODUCTION

It is known[1,2] that layered crystals in which the interatomic interactions in the planes of the layers are much stronger than between the layers have an unusual vibrational-spectrum structure. In the long-wave limit (acoustic branch) an important role is played in the dispersion law $\omega^2(\mathbf{k})$ of the oscillations polarized perpendicular to the plane of the layers, besides the terms quadratic in the wave vector, also by the higher terms of the expansion, which characterize the flexural rigidity of the individual atomic layer. In the limiting case of non-interacting layers, such oscillations are flexure waves propagating in the individual layers.

The thermal properties of layered structures, with allowance for the indicated peculiarities of the vibrational spectrum, were first considered theoretically by I. M. Lifshitz.[1] He has shown that the unusual character of the oscillation-dispersion law leads in the low-temperature region to anomalous of various thermal properties (the heat capacity, the coefficients of thermal expansion, etc.).

Singularities in the vibrational spectrum can be expected also in other phenomena that take place with participation of phonons.

We report here a theoretical and experimental study of spin-lattice relaxation in crystals with layered structure. Unusual temperature dependences are established for the times of the Raman spin-lattice relaxation, and are attributed to direct propagation of flexural waves in such crystals.

1. Theory

In layered crystals, the shear modulus μ in the planes xz and yz, and the Young modulus β along the z axis, are much less than the elastic moduli in the plane of the layer (the xy plane). Consequently the acoustic oscillations contain two branches polarized in the xy plane, and a third branch polarized along the z axis.[1,2] We represent the oscillation dispersion law, following[1], in the form

$$\omega_1{}^2=c_1{}^2\varkappa^2+\eta^2c^2k_z{}^2,\qquad \omega_2{}^2=c_2{}^2\varkappa^2+\eta^2c^2k_z{}^2,$$
$$\omega_3{}^2=\eta^2c^2\varkappa^2+\zeta^2c^2k_z{}^2+\gamma^2\varkappa^4, \tag{1}$$
$$\gamma=\frac{ca\nu}{\pi},\qquad \eta^2=\frac{\mu}{\rho c^2}\leqslant 1,\qquad \zeta^2=\frac{\beta}{\rho c^2}\ll 1,\qquad \nu\lessapprox 1.$$

Here c_1 and c_2 are the longitudinal and transverse sound velocities in the plane of the layer, $2/c = 1/c_1 + 1/c_2$, $\kappa^2 = k_x^2 + k_y^2$, and ρ is the density of the crystal. As seen from (1), the third branch of the oscillations has an anomalous dispersion law. In the limiting case $\eta \to 0$, $\zeta \to 0$, meaning a transition to non-interacting layers, the function $\omega_3(k)$ corresponds to flexural waves propagating in the individual layers.[3] An essential feature of this oscillation branch is the unusual character of the density of states $\varphi(\omega)$, which takes the form[2]

$$\varphi(\omega)\sim\begin{cases}\omega^2, & \omega\ll\eta^2\omega_D\\ \omega, & \eta^2\omega_D\ll\omega\ll\zeta\omega_D,\\ \text{const}, & \zeta\omega_D\ll\omega\ll\omega_D\end{cases} \tag{2}$$

ω_D is the Debye frequency. It follows from (2) that only at frequencies $\omega \ll \eta^2\omega_D$ is it possible to neglect the presence of the flexural rigidity of the individual layers.

Proceeding to the analysis of the role of the oscillations of a layered crystal in spin-lattice relaxation, we note first the case of direct processes. The temperature dependence of the rates of the direct relaxation processes, as is well known, does not depend on the explicit form of the dispersion law of the oscillations, but is determined only by the temperature dependence of the occupation numbers of the resonant phonons, and will therefore be of the usual type. At the same time, anomalies connected with the singularities of the state density (2) can appear in the field dependence of the rates of the direct processes.

In the case of Raman processes, the singularities in the state density, as will be shown below, lead to essential anomalies in the temperature dependences of the relaxation rates.

We consider Raman spin-lattice relaxation due to modulation of the intracrystalline field by the phonons. When considering a layered crystal, it is natural to assume that the crystal field acting on a magnetic center situated in some layer is determined mainly by the crystal atoms belonging to the same layer. The dynamic Hamiltonian of the spin-phonon interaction, which determines the times of the Raman spin-lattice relaxation, will be represented in the form

$$V=\sum_{i=1}^{4}R_iQ_i, \tag{3}$$

$$Q_1=(e_{xx}+e_{yy})^2,\quad Q_2=(e_{xx}-e_{yy})^2+4e_{xy}^2,$$
$$Q_3=(\partial u_z/\partial l)^2,\quad Q_4=(\partial^2u_z/\partial l^2)^2a^2. \tag{4}$$

We have assumed in (3) and (4) the long-wave approximation and the axial symmetry in the layer plane, a symmetry typical of layered structures; R_i includes the spin operators and the spin-phonon coupling constant; $e_{\alpha\beta}$ are the components of the strain tensor; $l^2 = x^2 + y^2$; a is the lattice constant in the plane of the layer.[1)] The variables Q_1 and Q_2 describe the deformations produced in the planes of the layers by the oscillation modes ω_1 and ω_2, and their plots are of the usual type. The variables Q_3 and Q_4 are connected with the displacements u_z due to the flexural oscillations. The distinguishing feature of the flexural oscillations is that in the approximation linear in the displacements they produce no changes in the relative dimensions in the plane of the layer. Modulation of the crystal field is due in this case only to the curvature that results from the inflexion and is determined by the second derivative of the z-component of the displacement (Q_4). The term containing Q_3 appears when account is taken in the strain-tensor components of the u_z-terms that are nonlinear in the displacements, and also when account is taken of the rocking (due to flexure) of the local symmetry axes inside the crystal field; this rocking can lead in a number of cases to spin-lattice relaxation.[4,5] The probability of the relaxation transitions between the spin levels a and b is equal to[2)]

$$W_{a\to b}=\frac{1}{\hbar^2}\sum_i|R_{iab}|^2\langle Q_i(t)Q_i\rangle_{\omega_{ab}}, \tag{5}$$

⟨...⟩ denotes averaging over the equilibrium ensemble of the phonons. Recognizing that

$$u_\alpha(r)=\sum_{ks}\left(\frac{\hbar}{2M\omega_s(k)}\right)^{1/2}(a_{ks}^+e^{ikr}+a_{ks}e^{-ikr})\lambda_\alpha^{(s)}, \tag{6}$$

where $\lambda_\alpha^{(s)}$ is the polarization vector of the s-th oscillation mode,

$$\lambda^{(1)}=(\cos\varphi,\ \sin\varphi,\ 0),\quad \lambda^{(2)}=(\sin\varphi,\ -\cos\varphi,\ 0),$$
$$\lambda^{(3)}=(0,\ 0,\ 1),\quad \varphi=\sphericalangle\varkappa\mathbf{x}, \tag{7}$$

we obtain ($\hbar\omega_{ab} \ll k_BT$)

$$\langle Q_i(t)Q_i\rangle_{\omega_{ab}}=\int_0^{\omega_D}d\omega[n(\omega)+1]n(\omega)\nu_i^2(\omega), \tag{8}$$

$$\nu_i(\omega)=\frac{\hbar}{(2\pi)^{3/2}\omega\rho}q_i\int\varkappa^{p_i}d\varkappa\int dk_z\delta[\omega-\omega_i(k)],$$
$$q_i=\begin{cases}1, & i=1,3\\ \sqrt{2}, & i=2,\\ a^2, & i=4\end{cases}\qquad p_i=\begin{cases}3, & i=1,2,3\\ 5, & i=4\end{cases}, \tag{9}$$

n(ω) are the Planck phonon numbers. Since the dispersion laws of the oscillations, in accord with (1) and (2), differ significantly in different frequency interval, the function $\nu_i(\omega)$ also has a complicated character. Carrying out the calculations with allowance for (7) and (1), and neglecting the inessential difference between the longitudinal and transverse sound velocities in the plane of the layer, we obtain

$$\nu_1(\omega)=\frac{2\hbar\omega^2}{(2\pi)^{3/2}\rho c^4}\begin{cases}{}^2/_3\,\omega/\eta c, & \omega\ll\eta\omega_D\\ \pi/b, & \eta\omega_D\ll\omega\ll\omega_D\end{cases} \tag{10}$$

$$\nu_3(\omega)=\frac{\hbar}{(2\pi)^{3/2}\rho\gamma^2}\begin{cases}4\omega^3/3\eta^4\zeta c^5, & \omega\ll\eta^2\omega_D\\ \omega/\zeta c, & \eta^2\omega_D\ll\omega\ll\zeta\omega_D,\\ \pi/b, & \zeta\omega_D\ll\omega\ll\omega_D\end{cases} \tag{11}$$

$$\nu_4(\omega)=\frac{\hbar\omega a^2}{(2\pi)^{3/2}\rho}\begin{cases}16\omega^4/15\eta^6\zeta c^7, & \omega\ll\eta^2\omega_D\\ \pi\omega/4\gamma^3\zeta c, & \eta^2\omega_D\ll\omega\ll\zeta\omega_D;\\ \pi/b\gamma^3, & \zeta\omega_D\ll\omega\ll\omega_D\end{cases} \tag{12}$$

here b is the lattice constant along the z axis.

Substituting (10)—(12) in (8) we obtain ultimately (Θ is the Debye temperature)

$$\langle Q_1(t)Q_1\rangle_{\omega_{ab}}={}^1/_2\langle Q_2(t)Q_2\rangle_{\omega_{ab}}$$
$$=\frac{12\hbar^2\pi^4}{\rho^2c^3a^5b^2}\begin{cases}\dfrac{120b^2}{9\eta^2a^2}\left(\dfrac{T}{\Theta}\right)^7, & T\ll\eta\Theta\\ (T/\Theta)^5, & \eta\Theta\ll T\ll\Theta\end{cases}, \tag{13}$$

$$\langle Q_3(t)Q_3\rangle_{\omega_{ab}}=\frac{\hbar^2}{4\rho^2\gamma^4\zeta}\begin{cases}\dfrac{8\cdot6!\pi^4}{9\eta^8\zeta c^3a^7}\left(\dfrac{T}{\Theta}\right)^7, & T\ll\eta^2\Theta\\ \dfrac{c}{\zeta a^3}\left(\dfrac{T}{\Theta}\right)^3, & \eta^2\Theta\ll T\ll\zeta\Theta,\\ \dfrac{c}{a^2b}\left(\dfrac{T}{\Theta}\right)^2, & \zeta\Theta\ll T\ll\Theta\end{cases} \tag{14}$$

$$\langle Q_4(t)Q_4\rangle_{\omega_{ab}}=\frac{\pi^5\hbar^2a}{(2\pi)^3\rho^2}\begin{cases}\dfrac{1{,}1\cdot10!\pi^6}{\eta^{12}\zeta^2c^3a^8}\left(\dfrac{T}{\Theta}\right)^{11}, & T\ll\eta^2\Theta\\ \dfrac{3}{2}\dfrac{\pi^2c^3}{\gamma^6\zeta^2a^2}\left(\dfrac{T}{\Theta}\right)^5, & \eta^2\Theta\ll T\ll\zeta\Theta.\\ \dfrac{2c^3}{b^2\gamma^6}\left(\dfrac{T}{\Theta}\right)^3 & \zeta\Theta\ll T\ll\Theta\end{cases} \tag{15}$$

In the region T ≫ Θ, all correlators (13)—(15) have the same temperature dependence, which does not differ from the usual $\sim T^2$. From (13)—(15) it is seen that allowance for the singularities of the phonon spectrum of a layered crystal causes the temperature dependences of the rates of Raman relaxation to differ noticeably from the analogous quantities for an isotropic crystal,[6] where we have $W_{ab} \sim T^7$ in the temperature region T < Θ. Let us compare the contributions made to the relaxation rates by the different phonon branches. The phonon branches ω_1 and ω_2 make the contribution (13) to the relaxation, whereas the flexural branch of the oscillations causes the contributions (14) and (15). Let us find the ratios of (13) to (14) and (15) in the actual temperature region ζΘ < T < Θ:

$$\frac{\langle Q_1(t)Q_1\rangle_{\omega_{ab}}}{\langle Q_3(t)Q_3\rangle_{\omega_{ab}}}\approx50\zeta\left(\frac{T}{\Theta}\right)^3\ll1,\quad\frac{\langle Q_1(t)Q_1\rangle_{\omega_{ab}}}{\langle Q_4(t)Q_4\rangle_{\omega_{ab}}}\approx\frac{1}{2}\left(\frac{T}{\Theta}\right)^2\ll1. \tag{16}$$

Consequently, in this temperature interval at R_1, R_2 ~ R_3, R_4 the contribution of the flexural branch is decisive. It can be shown on the basis of (13)—(15) that the contribution of the flexural oscillations is decisive in the temperature region T < ζΘ. The correlators corresponding to the variables Q_3 and Q_4 turn out to be approximately of the same order at ζΘ < T < Θ, and since they describe flexure-induced crystal-field changes that are different in character, the relative importance of any of the mechanisms will depend essentially on the relative values of R_3 and R_4.

2. Experiment

The temperature dependence of the spin-lattice relaxation in layered crystals was investigated by us in two types of experiments: a) ESR of Mn^{2+} in the layered crystal $CdBr_2$; b) nuclear relaxation in quadrupole nuclear resonance of the halide nuclei in the crystals $CdBr_2$, $CdI_2(4H)$, $PbI_2(4H)$, and $PbI_2(2H)$ (the abbreviation in the parentheses indicates the crystalline modification of the investigated crystals, for which polytypism is characteristic). The crystal structure of all the indicated compounds is made up by sandwiches consisting of a halide (X^-), a metal (Me^{2+}), and the X^-. The structure of the sandwiches was the same for all compounds, and the difference between the crystal structures of the compounds (or their different modifications) is expressed only in the different mutual placements of the sandwiches. The bond within the layer sandwiches is ion-covalent, whereas the bond between the sandwiches is of the Van der Waals type. The low-temperature thermal properties of the crystals of this class exhibit singularities that are characteristics of layered systems.[7] Although radiospectroscopic investigations of a number of layered crystals were carried out in[8,9] and elsewhere, the temperature dependence of the relaxation times was hitherto not investigated.

a) The temperature dependence of the spin-lattice relaxation of the ESR of Mn^{2+} was investigated in single crystals with Mn^{2+} concentrations 0.1 and 0.01 % mol. The ESR of Mn^{2+} in $CdBr_2$ is described by a trigonal spin Hamiltonian, the D constant of which undergoes a strong temperature dependence at $T > 10°K$. Questions involved in the temperature dependence of the spin-Hamiltonian constants in layered crystals were considered earlier.[10] The relaxation time T_1 was measured by the pulsed saturation method in the temperature interval 4.2–20°K.

The measurements performed on different lines of the fine and hyperfine structure of the spectrum have shown that the reconstruction of the ESR signal is described in all cases by a single-exponential function with one and the same time T_1. No concentration dependence of the time T_1 was observed. The experimental results are shown in Fig. 1, from which it follows that in the region $T \leq 9°K$ the spin-lattice relaxation time is inversely proportional to the temperature (direct process), whereas in the region $T > 10°K$ a relation $T_1 \sim T^{-(3.2 \pm 0.2)}$ is observed. At $T > 17°K$, it was impossible to carry out the measurements because the power of the saturating pulse was insufficient. The measurements of the spin-lattice relaxation of Mn^{2+} in $CdI_2(4H)$ have shown that the relaxation time at $T = 4.2°K$ is shorter by one order of magnitude than in the case of $CdBr_2$.

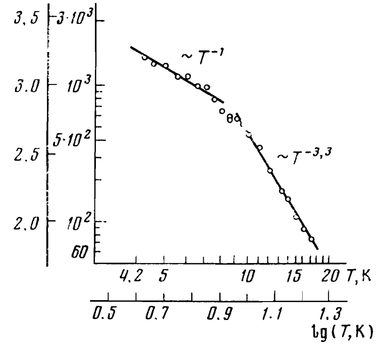

FIG. 1. Temperature dependence of the spin lattice relaxation time of ESR of Mn^{2+} in $CdBr_2$.

b) Pure quadrupole nuclear magnetic resonance (NQR) was investigated by the spin-echo method using an installation of the IS-3 type in the temperature interval 5–300°K, on both polycrystalline and single-crystal samples. Since nuclear relaxations can be due in many cases to the presence of paramagnetic impurities, the measurements were performed on samples with various degrees of purity. The agreement between the experimental results indicates that we are dealing here with a true nuclear spin-lattice relaxation, and not with relaxation via impurities. For the nuclei Br^{81} ($I = 3/2$) we investigated the single transition $3/2 \leftrightarrow 1/2$, and for the nuclei I^{127} ($I = 5/2$) we investigated only the transition $5/2 \leftrightarrow 3/2$. In $CdBr_2$ and in the 2H modifications of CdI_2 and PbI_2, all the halide ions are chemically equivalent, whereas in the 4H modification there are two nonequivalent positions, causing a doublet of the NQR line. The value of T_1 for both components of the doublet is practically the same. The transverse relaxation time T_2 in all the investigated samples is practically independent of temperature. The frequencies at which the NQR transitions were registered depend on the temperature and as the temperature is varied from 5 to 300°K the frequency ranges are 14.1–14.4, 28.4–29.5, and 11.2–7.2 MHz for $CdBr_2$, CdI_2, and PbI_2, respectively.

The results of the measurements of the temperature dependence of the time T_1 are shown for all substances in Fig. 2. It is seen that for all the samples one observes at $T > 50–70°K$ the relation $T_1 \sim T^{-2}$, which is usual for Raman phonon relaxation, whereas for $T < 50°K$ one observes relations close to $T_1 \sim T^{-3}$ (more accurate values of the exponents and the limits of errors are indicated in the callouts of the figure).

CONCLUSION

The investigated crystals agree to a sufficient degree with the assumptions made in the theoretical part of the paper. Direct calculation of the intracrystalline fields in the point-charge model shows that the main contribution

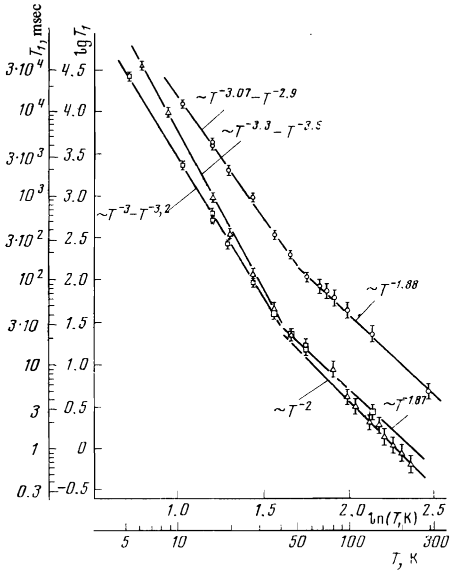

FIG. 2. Temperature dependences of the spin-lattice relaxation times: □–I^{127} in PbI (2H) and (4H); △–I^{127} in CdI_2 (4H), and ○–Br^{81} in $CdBr_2$.

to the axial field components is determined by the ions from the same layer sandwich in which the considered ion is located. Unfortunately, we have no data for the coefficients η and ζ, but the layered character of the crystals is very clearly pronounced, so that we can assume these coefficients to be small enough. The values of Θ for all the investigated crystals have not been established accurately, but for CdI_2 we have $\Theta \approx 150°K$,[7] and it can be assumed that for the remaining crystals this quantity is of the same order.

Comparing the results of the experiment with theory, and recognizing that $T_1^{-1} \sim W_{ab}$, we can state, substituting (13)—(15) in (5), that the observed unusual temperature dependence of T_1 ($T_1 \sim T^{-3}$) corresponds quite well with the temperature dependences of the contributions made to the relaxation by the flexures of the plane of the layer (Q_4). The direct process observed at low temperatures (ESR) and the quadratic temperature dependence of the relaxation probability at $T \gtrsim 0.5\Theta$ do not contradict the theory.

We can thus regard it as established that the decisive role is played in the spin-lattice relaxation of layered crystals by the flexural oscillations.

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1)The quantity a^2 has been introduced in Q_4 to preserve the dimensionality.

2)The calculation for the case of Kramers doublets must be modified somewhat.

[1] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **22**, 4, 471, 475 (1952).

[2] A. M. Kosevich, Osnovy mekhaniki kristallicheskoĭ reshetki (Principles of Crystal Lattice Mechanics), Nauka, 1972, Sec. 6.

[3] L. D. Landau and E. M. Lifshitz, Teoriya uprugosti (Theory of Elasticity), Nauka, 1965, Chap. 3 [Pergamon, 1971].

[4] T. Kushida, J. Sci. Hiroshima Univ. **19**, 327 (1955).

[5] B. S. Grechishkin, Yadernye kvadrupol'nye vzaimodeĭstviya v tverdykh telakh (Nuclear Quadrupole Interactions in Solids), Nauka, 1973, Chap. IV.

[6] S. A. Al'tshuler and B. M. Kozyrev, Elektronnyĭ paramagnitnyĭ rezonans soedineniĭ elementov perekhodnykh grupp (Electron Spin Resonance of Compounds of Transition-Group Elements), Nauka, 1972, Chap. V.

[7] E. S. Itskevich and P. G. Strelkov, Zh. Eksp. Teor. Fiz. **32**, 467 (1957) [Sov. Phys.-JETP **5**, 394 (1957)].

[8] C. G. Windsor, J. H. S. Griffiths, and J. Owen, Proc. Phys. Soc. **81**, 373 (1963).

[9] R. G. Barnes, S. L. Segel, and W. H. Jones, J. Appl. Phys., Suppl. **1**, 33, 296 (1962).

[10] M. D. Glinchuk, V. E. Goncharuk, D. L. Lyfar', and S. M. Ryachenko, Fiz. Tverd. Tela (in press).

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