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Electron spin-lattice relaxation in a paramagnet at high pressures

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Experimental results are presented on the variation of the electron spin-lattice relaxation time of a paramagnet during hydrostatic compression of the crystal. A significant effect of deformation on the relaxation process is discovered. It is shown that the relaxation transitions of two different magnetic ions can be bypassed by applying hydrostatic compression changing thereby the spin energy level system.

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1. INTRODUCTION

Studies of the EPR spectra of paramagnetic crystals subjected to an isotropic deformation at both high[1] and low[2,3] temperatures showed that external hydrostatic pressure gives rise to a fundamental change of the static properties of the crystal field, in particular, to a change of the symmetry type. The dynamics of the interaction of spin systems with a lattice is determined by the mechanism of the relaxation processes. The latter are characterized quantitatively by the electron spin-lattice relaxation time in paramagnetic crystals. This raises naturally another question concerning the effect of isotropic deformation on the dynamic parameters of the spin system: do the direct and Raman processes change (and to what extent) when the crystal is strongly deformed and the vibrational modes are correspondingly modified?

A paramagnetic cobalt ion (Co^{2+}) implanted as a regular impurity in the trigonal lattice of diamagnetic zinc fluosilicate was selected for the experiments. The choice of the Co^{2+} ion was dictated by the following considerations: first, the low level at which EPR is observed has a minimal twofold spin degeneracy, and, second, the electron relaxation of the Co^{2+} ion at low temperatures and normal pressure is described by both direct and Raman processes.[4]

2. MEASUREMENT TECHNIQUE

Since the data obtained here are, to the authors' knowledge, the results of the first experimental investigation of the electron spin-lattice relaxation at high pressures, a brief description of the distinguishing features of the measurement procedure is given below.

Optically homogeneous single crystals of zinc fluosilicate $ZnSiF_6 \cdot 6H_2O$ grown from the solution by the temperature reduction method (in the temperature range 45–28 °C) were used to investigate the effect of high pressures on the electron spin-lattice relaxation of Co^{2+} ions. The spin-relaxation measurements were carried out with an EPR pulsed relaxometer in the 3 cm band at pressures up to 13 kbar. The EPR signal was saturated with an additional klystron connected in the microwave circuit and tuned to the signal-generator frequency. Complete saturation of the EPR lines was attained at all pressures.

Since measurements of the spin-lattice relaxation time have their own distinctive features, that is: a) the

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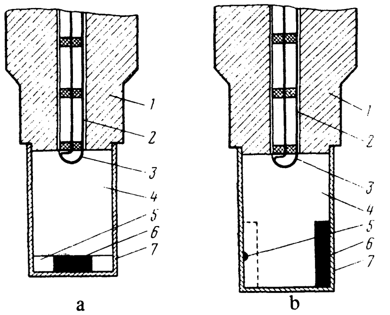

a b

FIG. 1. Cylindrical (a) and rectangular (b) leucosapphire resonators for measuring spin-lattice relaxations at high pressures: 1—plug head, 2—coaxial line with a coupling loop, 3—hemispherical cavity in the resonator body, 4—leucosapphire resonator, 5—leucosapphire washer, 6—investigated sample, 7—electrolytic copper cup; for the rectangular resonator the call-outs are the same, but 5—DPPH sample. A slot in the resonator for the second sample is shown by the dashed lines.

coupling of the microwave circuit and resonator must be below critical, and b) there must be no perturbing effect of the high-intensity EPR signals, we had to forgo the use of either crystal-resonators[5] or ceramic-based solid-state resonators that contained EPR impurities.[6]

Cylindrical and rectangular resonators (Fig. 1) were designed and made from pure leucosapphire for the 3-cm wavelength range. They were inserted into corresponding thin-walled electrolytic-copper cups. The same design was used for the pressure seals and for the resonator mounts, with the resonator cup fitting tightly over the protruding part of the plug. Optical matching of the contacting surfaces of the resonator end face and the plug head ensures a reliable pressure seal and makes it possible to obtain a low-pressure region in the inner channel of the plug and in the hemispherical cavity of the resonator body. A thin coaxial line with a coupling loop can move freely in this low-pressure region. The necessary coupling is achieved by changing the depth of its insertion into the resonator, while rotation of the loop changes the direction of polarization. The cylindrical leucosapphire resonator (Fig. 1a) operates in the H_{111} mode. The sample is placed in a leucosapphire washer at the bottom of the resonator. The samples were small cylinders with diameter somewhat smaller than the inside diameter (5–6 mm) of the 2-mm high washer. However, a sample of arbitrary configuration can be placed into the resonator as well.

When the angular dependence of the EPR spectrum is studied with the cylindrical resonators operating in the H_{11n} ($n = 1, 2, 3$) modes and with the sample placed at the bottom of the resonator the signal intensity changes. A rectangular resonator (Fig. 1b) operating in the H_{102} mode is free of this shortcoming. A step in the resonator body provides space for the sample. When the sample is placed in this manner, $\mathbf{H}_0 \perp \mathbf{H}_1$ and the signal intensity does not change as the magnetic field is rotated. With the rectangular resonator, two samples can be studied simultaneously, if required. For this purpose an additional step (shown in Fig. 1b by a dashed line) is cut on the opposite side of the resonator body.

The Q factor of the resonators at room temperature and frequency of 9.3 GHz is of the order of 3000. This enables the sensitivity of a standard EPR spectrometer to be reached. To restore the initial strength of the leucosapphire, the finished resonators were annealed after machining. It should be noted that the resonators can operate at higher pressures up to ~ 30 kbar as well.

The resonators described above were placed in a standard high pressure bomb.[7] A kerosene and oil mixture was used as the pressure-transmitting medium. The pressure was measured with a calibrated manganin gauge.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The ground state of the $Co^{2+}(3d^7)$ ion is ^4F. In the crystal field of zinc fluosilicate, the ground level is split into a singlet and two triplets, one of which is the ground one (Γ_4). Such an arrangement of the levels results in a strong effect of spin-orbit coupling on the electron spin-lattice relaxation. Hence, observation of EPR of Co^{2+} ions is possible only at low temperatures. Combined action of the spin-orbit and the low-symmetry component (trigonal, in this case) of the crystal field causes the lower level to be a Kramers doublet with an effective spin $S' = \frac{1}{2}$. The spectrum of the CO ion in such a field as described by the axially symmetric spin Hamiltonian[8]:

$$H_S = \beta[g_{\parallel} H_z S_z + g_{\perp}(H_x S_x + H_y S_y)] + A S_z I_z + B(S_x I_x + S_y I_y)$$

at $S = \frac{1}{2}$ and $I = \frac{7}{2}$, the g factors of Co^{2+} differ drastically from the pure spin g factor, and the anisotropy of the g factors can serve as a measure of the degree of distortion of the crystal-field cubic symmetry.

Due to the compressibility anisotropy of zinc fluosilicate, a water octahedron initially compressed along the [111] axis starts to level off when hydrostatic pressure is applied, thus decreasing the anisotropy of the g factors.[2] We studied the dependence of the spin-lattice relaxation time of the Co^{2+} ion in $ZnSiF_6 \cdot 6H_2O$ on the applied high pressure. The measurements were performed on samples with Co^{2+} concentration in the $ZnSiF_6 \cdot 6H_2O$ of the order of 0.1% (molar fractions of the cobalt fluosilicate in the zinc fluosilicate solution).

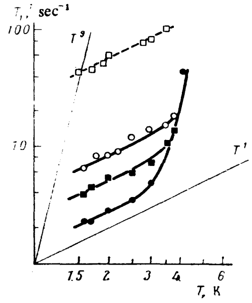

FIG. 2. Temperature dependences of the spin-lattice relaxation rate of Co^{2+} in $ZnSiF_6 \cdot 6H_2O$ at 9.3 GHz and at 0 (●), 1.7 (■), and 4.5 (○) kbar, as well as at a frequency of 25 GHz at pressure of 0 kbar (□).

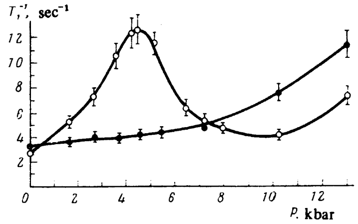

FIG. 3. Dependence of the spin-lattice relaxation rate of Co^{2+} in $ZnSiF_6 \cdot 6H_2O$ on the hydrostatic pressure at $T = 2$ K; ●—(−7/2; −7/2) transition; ○—(7/2; 7/2) transition.

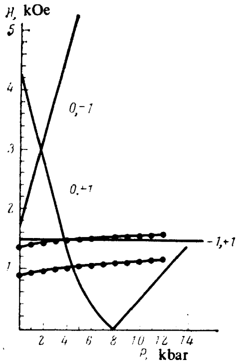

FIG. 4. Dependence of the resonance fields for the transitions Ni^{2+} ions (0, −1; 0, +1; −1, +1) and Co^{2+} ions ((●) upper curve—(7/2, 7/2) transition, lower curve—(−7/2, −7/2) transition) in $ZnSiF_6 \cdot 6H_2O$ on the hydrostatic pressure.

At this concentration of the paramagnetic centers the obtained intensities of the EPR signals are convenient for the measurements, and the spin-spin interactions that shorten the relaxation times do not appear. Nor does cross relaxation occur between the hyperfine structure lines. These remarks are based on the fact that the relaxation times obtained in this work and in[4], where the measured concentration is given (~ 0.01%), are very close. Besides, an analysis of the recovery curve showed that after saturation the intensity increases exponentially, and the relaxation time does not depend on the duration of the saturating pulse, which can vary over a wide range from 10^{-5} to $5 \cdot 10^{-2}$ sec.

Over the entire pressure range 0–13 kbar, we measured the temperature dependence of the spin-lattice relaxation time T_1. This dependence can be described by two processes: a direct process, with $T_1 = AT$ and a Raman process, with $T_1 \sim T^9$. Figure 2 illustrates the temperature dependences for three pressures at the frequency $\nu = 9$ GHz and the dependence of the direct process at normal pressure and at 25 GHz. If the frequency dependence of the direct process is assumed proportional to ν^n, then, in our case, $n = 3.2$. The difference between this exponent and the value predicted by Kronig-Van Vleck theory ($n = 4$) may be evidence of an admixture of another relaxation mechanism.

Figure 3 shows the variation of the direct-process relaxation rate at $T = 2$ K for two transitions of the hyperfine structure (hfs) with pressure (under the assumption that the hfs constant A is positive). Within the accuracy range of the experiment, no variations of the Raman-process relaxation rate were detected. It is seen that the curve for the strong-field transition (7/2; 7/2) has a pronounced extremum at 4.5 kbar. This extremal dependence of the strong-field transition relaxation rate is somewhat unusual compared with the smooth variation of the (− 7/2; − 7/2)-transition relaxation rate with pressure. The appearance of an extremum on the relaxation rate curve (Fig. 3) indicates that a new energy-transfer channel takes effect in the vicinity of the 4.5-kbar point. Such a channel can result from the presence of a spin system formed by another paramagnetic impurity with a shorter relaxation time. Thus, the levels of the alien spin system can bypass the Co^{2+}-ion energy levels in the vicinity of the 4.5-kbar point.

The assumption was verified that the Co^{2+} strong-field transition is bypassed because an uncontrollable impurity of some other ion in the same lattice was verified experimentally. A sample record of the EPR spectrum at maximal sensitivity in a wide range of magnetic fields showed that the crystal under study contained Ni^{2+} ions having a characteristic spectrum with three hyperfine structure lines at a concentration three orders of magnitude lower than that of cobalt. Since the relaxation time of Ni^{2+} ions at 2 K is significantly less (~ 2 msec) than the relaxation time of Co^{2+} ions (~ 300 msec), it is natural to assume that it is the Ni^{2+} ions that shorten the measured relaxation time of Co^{2+}. Figure 4, plotted according to the previously obtained data,[3,4] shows the pressure-induced change of the absorption lines in the magnetic field of the Ni^{2+} and Co^{2+} ions in zinc fluosilicate at 9 GHz. It is clearly seen that one of the three transitions, i.e., the forbidden Ni^{2+} (− 1; + 1) transition, is very weakly dependent on pressure and coincides with the (7/2; 7/2) Co^{2+} transition at 4.5 kbar. Measurements on crystals of $ZnSiF_6 \cdot 6H_2O$ with equal concentrations of Co^{2+} and Ni^{2+} ions on the order of 0.1% permitted visual observation of the shift of the Co^{2+} and Ni^{2+} absorption lines with pressure and their coincidence at about 4.5 kbar. The effective relaxation time of the coincided transitions was close to the relaxation time of the forbidden (+ 1; − 1) transition in the spectrum of Ni^{2+}.

If the bypassing effect is not taken into account, the behavior of the spin-lattice relaxation rates of the outermost hyperfine lines with pressure is similar and the general tendency is for relaxation rates to increase with pressure. The more pronounced growth of the relaxation rate in the pressure range 11–13 kbar seems to result from the appreciable broadening of the lines, from possible occurrence of the crossover mechanism, and also from onset of bypassing by allowed Ni^{2+} (0; + 1) transition at these pressures.

Thus, the main changes in the behavior of relaxation characteristics of Co^{2+} ions under pressure in zinc fluosilicate crystals are caused by the presence of an uncontrollable Ni^{2+} impurity in the crystals. The changes of the inherent relaxation of cobalt, however, at least at pressures up to ~ 7 kbar, are very insignificant and can indicate invariance of the spin-phonon interactions in this pressure range.

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Electron dispersion law in a bounded crystal

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The problem of calculating the dispersion law in a semi-infinite crystal (the Tamm problem) and in a film is formulated in the terms of envelopes and is solved analytically as applied to cubic semiconductors with narrow forbidden bands. The solution of the Tamm problem points to the existence of one two-dimensional Tamm subband. Depending on the surface properties, the extremum of this subband lies either in the forbidden band or coincides with the top of the valence band. In the latter case, the states in the Tamm subband are quasistationary. The dispersion curve in the Tamm subband is double-humped. The energy spectrum of the carriers in the film is analyzed and the existence of two-dimensional subbands of a new type (besides the usual Tamm and size-quantized ones) is predicted: 1) hybrid subbands to which states localized near the film boundaries as well as delocalized states correspond; 2) a pair of subbands with anomalously small masses, which realize the two-dimensional analog of the zero-gap state in a definite film-thickness interval. It is shown the effective masses at the bottom of the lower size-quantized subbands can differ substantially in thin films from their quasiclassical values. The most important of the foregoing results cannot be obtained within the framework of one-dimensional models of a bounded crystal or models that can be reduced to one-dimensional.

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1. INTRODUCTION

It is known[1–4] that size quantization leads to a splitting of each energy band in the conduction-electron spectrum into two-dimensional size-quantized subbands. In the classical approximation,[1] the dispersion law in the n-th subband ($n \gg 1$) can be obtained in the isotropic case from the condition

$$E=\varepsilon(\varkappa,\ \pi n/d), \tag{1}$$

where E is the electron energy, $\varkappa(\varkappa_x, \varkappa_y, 0)$ is the two-dimensional quasimomentum in the plane of the film, $k_z = \pi n/d$ is the quantized value of the transverse component of the quasimomentum, n is a positive integer, and d is the thickness of the film, the z axis coincides with the normal to the film, and $\varepsilon(\mathbf{k})$ is the electron dispersion in a perfect crystal.

The problem of calculating the spectrum of the electrons in a film at $n \sim 1$ is usually formulated in the language of envelopes, i.e., of functions that vary slowly over the lattice periods and are the effective wave functions of the electron in the crystal.

The boundary conditions that the envelopes must satisfy on the crystal surface have already been derived earlier.[5] In contrast to the null conditions,[3,4] these boundary conditions take into account the abruptness of the variation of the electron potential energy near the surface; this, as is well known,[6] is the cause of the appearance of surface (Tamm) states. The case $\varkappa = 0$ was considered and it was shown that the quasiclassical quantization rules $k_z = \pi n/d$ are valid only in sufficiently thick films. The deviation of $\varkappa$ from zero not only changes the system of equations for the envelopes,[7] but also renormalizes appreciably the boundary conditions. The latter is due to the face that the $\varkappa\hat{\mathbf{p}}$ interaction jointly with the potential of the boundary entangle the electron motions transverse and longitudinal relative to the surface. The result is that k_z becomes dependent on $\varkappa$.

The purpose of the present paper is to consider the case $\varkappa \neq 0$ and to determine the electron dispersion law in each subband—both the size-quantized band and the Tamm band. The work is based on a derivation of the boundary conditions for the envelopes (Sec. 2). The problem of determining the electron spectrum in a semi-infinite crystal (the Tamm problem, Sec. 3) or in a film (Sec. 4) then reduces to a solution of relatively simple equations for the envelopes with the obtained boundary conditions. The problem was solved for cubic semicon-

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