Spin-lattice relaxation and phonon "heating" effect in Co^{2+}-activated ZnS single crystals

S. A. Al'tshuler, I. N. Kurkin, Yu. K. Chirkin, and V. I. Shlenkin

Kazan' State University

(Submitted 16 May 1977)
Zh. Eksp. Teor. Fiz. 73, 1896–1902 (November 1977)

A report is given of the first experimental investigation of the field and concentration dependences of the spin–lattice relaxation times of an ion with $S > 1/2$ in a cubic field (Co^{2+} in ZnS). It is shown that at low Co^{2+} concentrations the spin–phonon interaction is in accordance with the van Vleck mechanism. At high concentrations, the relaxation is slowed down by the phonon "heating" effect. Estimates are obtained of the spin–phonon interaction parameters.

PACS numbers: 76.60.Es

1. INTRODUCTION

Much work has been done on the spin–lattice relaxation (SLR) of paramagnetic impurity centers in crystals (the subject has been reviewed in several papers[1–3]). It is usual to assume that the relaxation rate is governed mainly by the Van Vleck mechanism.[4,5] If the effective spin is $S=1/2$, we may take this to be proved experimentally because there have been many reports of experimental observations of the temperature (T), magnetic field (H), and concentration dependences of the relaxation time in accordance with the Van Vleck mechanism. However, in the case of systems with $S>1/2$, the important predictions of the theory of the Van Vleck mechanism that the rate of relaxation should be proportional to H^2 and there should be no dependence on the paramagnetic center concentration have not yet been proved experimentally.

In view of this situation, we undertook an investigation of the SLR of cubic Co^{2+} centers in ZnS single crystals. The system seemed to be very suitable for the purpose in question because of the following factors.

a) The ESR spectrum of the system is extremely simple. The immediate environment of a Co^{2+} ion consists of a tetrahedron of S^{2-} ions in whose crystal field (of T_d symmetry) the lowest level of $Co^{2+}(3d^7, {}^4F)$ is an orbital singlet. The application of a magnetic field splits this level into four equidistant sublevels (Fig. 1). The absence of a fine structure and the very weak hyperfine structure are responsible for the fact that the ESR spectrum at frequencies ≤ 15 GHz consists of just one line. Data on the ESR of the cubic Co^{2+} centers in ZnS are given by Ham *et al.*[6]

b) The cubic symmetry is simplest for calculations.

c) The presence of a strong spin–phonon interaction (the results will be given below) allows us to ignore a possible influence of other impurities on the SLR times.

d) The strong spin–phonon interaction leads us to expect that the system in question should make it possible to investigate also the phonon "heating" effect.

2. EXPERIMENTAL RESULTS

We measured the SLR times of the cubic Co^{2+} centers in ZnS. Information on the mechanisms responsible for these relaxation times was found by making measurements as a function of the temperature (1.5–4.2 °K), concentration ($4.5\times10^{17}-1.3\times10^{19}$ ions/cm^3), and frequency (~9.4 and ~15.0 GHz).

At the frequency of ~15.0 GHz the relaxation times were measured by the method of pulse saturation of the ESR signal and at ~9.4 GHz they were determined by the method of saturation of the electron spin echo signal. The results of the measurements are given in Fig. 2.

In the concentration range from 4.5×10^{17} to 4.6×10^{18} ions/cm^3 the relaxation time T_1 was independent of the concentration and was described satisfactorily by the following formula:

$$T_1^{-1}=2.8\cdot10^{-4}H^2T. \qquad (1)$$

The value of T_1 was independent, within the limits of the experimental error, of the direction of an external magnetic field relative to the crystallographic axes, and the kinetics of recovery of the ESR signal was exponential.

When the concentration was $n=1.3\times10^{19}$ ions/cm^3 and the frequency was ~9.4 GHz, the ESR recovery curve was not exponential but it could be described satisfactorily by a sum of two exponential functions. A narrow initial part of the recovery curve had a relaxation time close to T_1 but the main part of the curve was charac-

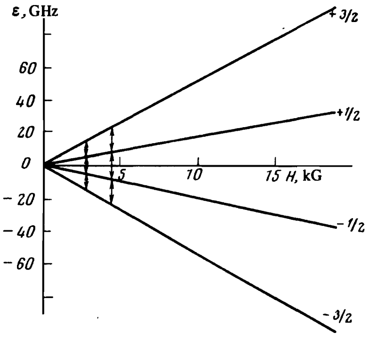

FIG. 1. Behavior of energy levels of cubic Co^{2+} centers in ZnS crystals in a magnetic field. The arrows represent the experimentally observed transitions at frequencies ~9.4 GHz and ~15.0 GHz.

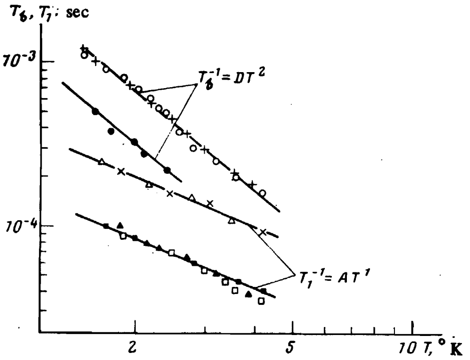

FIG. 2. Relaxation times of cubic Co^{2+} centers in ZnS crystals in the temperature range 1.6–4.2 °K: ○) $n=1.3\times10^{19}$ ions/cm^3, $\nu\sim9.4$ GHz, $l\sim1.3$ mm; +) $n=1.3\times10^{19}$ ions/cm^3, $\nu\sim15.0$ GHz, $l\sim1.3$ mm; ●) $n=1.3\times10^{19}$ ions/cm^3, $\nu\sim15.0$ GHz, $l\sim0.9$ mm; △) $n=2.8\times10^{18}$ ions/cm^3, $\nu\sim9.4$ GHz; ▲) $n=2.8\times10^{18}$ ions/cm^3, $\nu\sim15.0$ GHz; ×) $n=1.4\times10^{18}$ ions/cm^3, $\nu\sim9.4$ GHz; □) $n=4.6\times10^{18}$ ions/cm^3, $\nu\sim15.0$ GHz; ■) $n=4.5\times10^{17}$ ions/cm^3, $\nu\sim15.0$ GHz.

terized by the time constant T_b. The relaxation time T_b was independent of the frequency and described by

$$T_b^{-1}=3.3\cdot10^2T^2=DT^2. \tag{2}$$

Moreover, T_b was independent of the size of the sample, as found at ~15 GHz. Unfortunately, the very small amount of the investigated substance available to us (~30 mg) prevented us from investigating regular samples with well-controlled dimensions. We had two single crystals of arbitrary shape with the smallest dimensions $l\sim1.3$ mm and $l\sim0.9$ mm, and also a powder of ~0.6 mm and ~0.1 mm grain size. The inaccuracy in the determination of the dimensions of the samples prevented us from drawing reliable conclusions on the functional dependence on the size (of the kind investigated in detail elsewhere[7,8]) but we could definitely say that a reduction in the dimensions reduced also the relaxation time which tended to a value obtained for samples with low concentrations. The results for the 1.3×10^{19} ions/cm^3 concentration are given in Fig. 2 only for the samples with $l\sim1.3$ mm and $l\sim0.9$ mm so as not to confuse the picture. The relaxation times for $l\sim0.6$ mm and $l\sim0.1$ mm at $T\sim1.6$ °K were found to be ~300 μsec and ~200 μsec, respectively. The expression (2) described the sample with $l\sim1.3$ mm.

3. DISCUSSION OF RESULTS

The temperature and frequency dependences of the relaxation times were very different for the samples with low and high paramagnetic center concentrations. Therefore, we shall discuss these two cases separately.

A. Low concentrations

The absence of a concentration dependence and the nature of the temperature and magnetic field dependences given by Eq. (1) are very convincing evidence that the most effective relaxation mechanism in the range of concentrations 4.5×10^{17}–4.6×10^{18} ions/cm^3 is the Van Vleck mechanism, and that the relaxation is due to one-phonon (direct) processes. It is worth noting the short relaxation times (even at 2 °K, we have $T_1\approx10^{-4}$ sec). We shall carry out a theoretical analysis of the experimentally determined relaxation times. The expression for the transition probability in the case of direct processes is[9]

$$A_{mm'}^{(1)}=\frac{8\pi^3kv^2T}{h^2\rho v^5}\Phi_{mm'}=\frac{8\pi^3kg^2\beta^2H^2T}{h^4\rho v^5}\Phi_{mm'}, \tag{3}$$

where

$$\Phi_{mm'}=\frac{1}{3}\sum_{\gamma,\delta}|\langle m|W_{\gamma,\delta}|m'\rangle|^2. \tag{4}$$

In the $S>1/2$ case the quantity $W_{\gamma,\delta}$ is essentially given by the following expression:

$$W_{\gamma,\delta}=\frac{1}{2}\sum_{\alpha,\beta}G_{\alpha\beta\gamma\delta}(S_\alpha S_\beta+S_\beta S_\alpha). \tag{5}$$

Bearing in mind that in the T_d symmetry there are only two independent spin–phonon interaction constants, G_{11} and G_{44},[9] and that such a system of levels with $S=3/2$ can be described by two time constants, τ_1 and τ_2,[10] we can write down the following expressions for the relaxation rates in the case of an arbitrary orientation of the external magnetic field:

$$\frac{1}{\tau_1}=A_{mm'}^{(1)}(\Delta m=1)=K\left[\frac{27}{2}G_{11}^2+\left(3G_{44}^2-\frac{27}{2}G_{11}^2\right)(n_1^4+n_2^4+n_3^4)\right]H^2T, \tag{6}$$

$$\frac{1}{\tau_2}=A_{mm'}^{(1)}(\Delta m=2)=K\left[\frac{27}{8}G_{11}^2+\frac{9}{4}G_{44}^2+\left(\frac{27}{8}G_{11}^2-\frac{3}{4}G_{44}^2\right)\times(n_1^4+n_2^4+n_3^4)\right]H^2T, \tag{7}$$

where

$$K=8\pi^3kg^2\beta^2/3h^4\rho v^5, \tag{8}$$

and n_1, n_2, and n_3 are the direction cosines of the external magnetic field relative to the crystallographic axes x, y, and z.

It follows from Eqs. (6) and (7) that for

$$G_{11}^2={}^2/_9G_{44}^2 \tag{9}$$

there should be no orientational dependence of the relaxation times and then $\tau_1=\tau_2$, i.e., we have a situation found experimentally. The expression for the relaxation rate then becomes

$$1/\tau=3KG_{44}^2H^2T. \tag{10}$$

Taking $\rho=4.1$ g/cm^3 (Ref. 11), $v=2.8\times10^5$ cm/sec (Ref. 11), and $g=2.25$ (Ref. 6), we find that

$$1/\tau=4.2\cdot10^{-8}G_{44}^2H^2T. \tag{11}$$

In describing the experimental results by means of Eq. (1) subject to Eq. (9), we have to assume that

$$|G_{11}|=38.5\,\mathrm{cm}^{-1},\quad|G_{44}|=81.8\ \mathrm{cm}^{-1}. \tag{12}$$

We shall now compare our data on the SLR times of Co^{2+} in ZnS with other matrices in which the impurity ion has the spin $S=3/2$. For example, the rate of relaxation of Cr^{3+} in Al_2O_3 at ~9 GHz for such concentrations that T_1 is independent of the concentration[11] is 2×10^3 times less than for Co^{2+} in ZnS. This difference is explained satisfactorily by a reduction in the parameters of the spin–phonon interaction, which are proportional to the ratio λ/Δ (λ is the spin–orbit interaction constant equal to 87 cm^{-1} for Cr^{3+} and 180 cm^{-1} for Co^{2+}[9]; Δ is the position of an excited orbital triplet, which is 3850 cm^{-1} for Co^{2+} in ZnS[12] and ~17 000 cm^{-1} for Cr^{3+} in Al_2O_3[13]); the difference can also be explained by an increase in the velocity of sound which is 7.02×10^5 cm/sec in Ref. 11. The quantity $(\lambda/\Delta)^2 v^{-5}$ decreases by a factor of ~10^4 from $ZnS:Co^{2+}$ to $Al_2O_3:Cr^{3+}$, which is in good agreement with the experimental results. However, one should point out that the Cr^{3+} ions in Al_2O_3 are in a field of trigonal symmetry and the spin–phonon interaction parameters are considerably greater,[14] which restricts greatly the scope of the comparison with Co^{2+} in ZnS.

The spin–lattice relaxation of ions with $S=3/2$ in a cubic field has been investigated in the following systems: $MgO:Er^{3+}$,[10] $CaF_2:Nd^{3+}$, $CaF_2:Dy^{3+}$,[15] $KZnF_3:Er^{3+}$,[16] and $MgO:Cr^{3+}$.[17] In the case of the rare-earth elements the relaxation times depend on the orientation of an external magnetic field and amount to 10^{-3}–10^{-5} sec at helium temperatures. The order of magnitude of the relaxation times is still described satisfactorily by Eqs. (6)–(8) but we must bear in mind that the relaxation rate increases by a factor of $(\lambda/\Delta)^{-2}\approx100$ compared with the $ZnS:Co^{2+}$ because of an increase in the spin–phonon interaction parameters and we must also remember that the rate of relaxation decreases approximately by two orders of magnitude because the velocity of sound in MgO, CaF_2, and $KZnF_3$ crystals is 2–3 times higher[11] than in ZnS. The relaxation times of Cr^{3+} in MgO are 10^{-1}–10^0 sec, i.e., they are four orders of magnitude longer than for Er^{3+} in MgO, which is explained by the fact that in the case of Cr^{3+} in MgO we have $(\lambda/\Delta)^{-2}\approx10^4$.

B. High concentrations

The quadratic temperature dependence, increase in the relaxation time with rising concentration of the paramagnetic centers, absence of a frequency dependence, and reduction in the relaxation times with decreasing dimensions of a sample all indicate that for $n=1.3\times10^{19}$ ions/cm³ the relaxation occurs under phonon "heating" conditions.[5,18] Using the experimental value of the parameter D [see Eq. (2)] and the expression[18]

$$D=48\pi k^2\Delta\nu/v^3h^2nT_{ph}, \tag{13}$$

where $\Delta\nu$ is the ESR line width amounting to ~100 MHz, we can determine the resonance phonon lifetime which is $T_{ph}\approx0.9\times10^{-7}$ sec. This value is in good agreement with the assumption that the phonon lifetime is governed by the scattering on the boundaries of a crystal: in the case of a sample of l~1.3 mm size we have $T_{ph}\sim l/2v\approx2.3\times10^{-7}$ sec.

The phonon heating effect was observed by us only for a sample of ZnS with the purely cubic structure (sphalerite). In the case of the samples containing also an admixture of the hexagonal phase ZnS (wurtzite), there was no phonon heating in spite of the high concentration of the cubic Co^{2+} centers ($\gtrsim10^{19}$ ions/cm³). It should also be noted that the $ZnS:Co^{2+}$ sample exhibiting the phonon heating effect was of very high quality, as indicated by its ESR spectrum: this was the only crystal at our disposal which exhibited a hyperfine structure in spite of the fact that this structure was very weak.[6]

Up to now, the phonon heating effect (also known as the phonon bottleneck) in the saturation of the ESR signal has been largely observed for systems with an effective spin $S=1/2$ but not for systems with $S=3/2$ in cubic fields. The case investigated by us is interesting for the following reasons:

1) the Zeeman splitting of Co^{2+} in ZnS is equidistant, so that ESR line saturation can be used to equalize the populations of all the spin levels;

2) the spin–phonon interaction of Co^{2+} in ZnS is very strong, which facilitates fast heating of resonance phonons (it should be noted that in previous investigations of the spin–lattice relaxation of a quartet of levels[10,15,16] the relaxation times have been found to be short; clearly, such systems are suitable for the realization of the phonon bottleneck effect and investigation of such phenomena);

3) the phonon bottleneck effect in a system of equidistant levels with $S=3/2$ should give rise to two strong hot-phonon bands in the range of frequencies corresponding to the transitions $\frac{3}{2}\to\frac{1}{2}$, $-\frac{1}{2}\to\frac{3}{2}$ and $\frac{3}{2}\to-\frac{1}{2}$, $\frac{1}{2}\to-\frac{3}{2}$.

4. CONCLUSIONS

The present paper reports the first investigation of an ion with $S=3/2$ in a cubic field, carried out at various frequencies and in a wide range of concentrations.

The relatively short Van Vleck relaxation times are clearly typical of such systems. On the one hand, this provides favorable conditions for the observation of the true relaxation times, since the influence of other impurities can be ignored, and, on the other, conditions for the appearance of the phonon heating effect are easily satisfied. Both situations were observed experimentally for various Co^{2+} concentrations in ZnS crystals.

It would be interesting to carry out a more detailed investigation of the phonon heating effect in the system under consideration. This would require measurements on samples with control dimensions at temperatures below 1 °K. It would be very illuminating to carry out experiments involving recording of phonons of doubled frequency.

The role of other processes in the spin–lattice relaxation can be illustrated by measurements at temperatures above 4 °K.

The authors are grateful to A. I. Ryskin for supplying the investigated single crystals and to V. D. Korolev for discussing our results.

[1] K. J. Standley and R. A. Vaughan, Electron Spin Relaxation Phenomena in Solids, Adam Hilger, London, 1969.
[2] R. Orbach and H. J. Stapleton, in: Electron Paramagnetic Resonance (ed. by S. Geschwind), Plenum Press, New York, 1972, p. 121.
[3] J. C. Gill, Rep. Prog. Phys. 38, 91 (1975).
[4] J. H. Van Vleck, Phys. Rev. 57, 426 (1940).
[5] J. H. Van Vleck, Phys. Rev. 59, 724 (1941).
[6] F. S. Ham, G. W. Ludwig, G. D. Watkins, and H. H. Woodbury, Phys. Rev. Lett. 5, 468 (1960).
[7] F. R. Nash, Phys. Rev. Lett. 7, 59 (1961).
[8] V. D. Korolev, S. A. Peskovatskiĭ, and V. M. Shul'ga, Fiz. Tverd. Tela (Leningrad) 17, 3113 (1975) [Sov. Phys. Solid State 17, 2063 (1975)].
[9] S. A. Al'tshuler and B. M. Kozyrev, Elektronnyĭ paramagnitnyĭ rezonans soedineniĭ élementov promezhutochnykh grupp (Electron Paramagnetic Resonance of Compounds of Intermediate Group Elements), Nauka, M., 1972.
[10] M. Borg, R. Buisson, and C. Jacolin, Phys. Rev. B 1, 1917 (1970).
[11] O. L. Anderson, in: Physical Acoustics: Principles and Methods (ed. by W. P. Mason), Vol. 3, Part B, Academic Press, New York, 1965, p. 43 (Russ. transl., Mir, M., 1968).
[12] P. Koidl, O. F. Schirmer, and U. Kaufmann, Phys. Rev. B 8, 4926 (1973).
[13] D. T. Sviridov, R. K. Sviridova, and Yu. F. Smirnov, Opticheskie spektry ionov perekhodnykh metallov v kristallakh (Optical Spectra of Transition Metal Ions in Crystals), Nauka, M., 1976.
[14] P. L. Donoho, Phys. Rev. 133, A1080 (1964).
[15] N. E. Kask, L. S. Kornienko, and M. Tabak, Fiz. Tverd. Tela (Leningrad) 13, 46 (1971) [Sov. Phys. Solid State 13, 36 (1971)].
[16] A. A. Antipin, A. F. Klimachev, S. L. Korableva, L. D. Livanova, and A. A. Fediĭ, Fiz. Tverd. Tela (Leningrad) 17, 1042 (1975) [Sov. Phys. Solid State 17, 664 (1975)].
[17] J. G. Castle, Jr. and D. W. Feldman, Phys. Rev. 121, 1349 (1961).
[18] P. L. Scott and C. D. Jeffries, Phys. Rev. 127, 32 (1962).

Translated by A. Tybulewicz

Strain-texture transition in type-A smectics

P. V. Adomenas, L. K. Vistin', A. N. Mesropyan, A. A. Tubelite, I. G. Chistyakov, S. P. Chumakova, V. M. Eigenbrot, and S. S. Yakovenko

Crystallography Institute, USSR Academy of Sciences

(Submitted 19 May 1977)
Zh. Eksp. Teor. Fiz. 73, 1903–1910 (November 1977)

To explain the physical nature of the transition of the homotropic smectic texture into a confocal one, we investigated the mechano-optical characteristics in smectic liquid crystals. A mechano-optical hysteresis is observed in smectics of type *A*. An experimental setup capable of investigating the mechano-optical effects in liquid crystals is described. The transition of the homotropic structure into a confocal one, due to stretching of the smectic layer, is investigated in detail. It is shown that this transition is from one texture into another, and is not a phase transition. This texture transition is responsible for the observed mechano-optical hysteresis. It is established that both textures, the homotropic and the confocal, are stable for the smectic type-*A* phase.

PACS numbers: 64.70.Ew, 61.30.Eb, 78.20.Hp

A smectic liquid crystal of type A has a layered structure in which the long axes of the molecules are perpendicular to the layers, whose thicknesses are of the order of the molecule length, 20–30 Å. The optical properties of smectic-A are analogous to the optical properties of a solid uniaxial crystal. The mechanical properties have a large anisotropy. Thus, the elasticity measured perpendicular to the layers is closer to the elasticity of the solid crystal, while the elasticity measured along the layers is similar to the elasticity of the nematic liquid crystal.

Delaye *et al.*[1] and Clark and Meyer[2] have reported observation of mechanical instability in smectic A, wherein flexure of the smectic layer with a definite period takes place. The instability appeared at small strains, lower than a certain critical value. The flexure relaxation time was of the order of several milliseconds. The reason for the instability is that the tensile force that tends to separate the smectic layers is balanced by the wavy distortion that is produced in the layer. It was noted in the cited papers that tensile strains exceeding the critical value lead to a transition from the homotropic texture to a texture that consists of bright regions—domains. The relaxation time of such a domain texture is long, on the order of a minute. The causes of the appearance of the domain structure at large strains were, however, not considered in[1,2]. We shall henceforth call the transition into a domain texture a strain-texture transition (STT).

STT were later observed in a new class of smectics of type A,[3,4] which are obtained when two nematics are mixed. These systems offer the advantage that they are in the smectic liquid-crystal phase at room temperature.

To investigate the STT we developed the experimental setup shown in Fig. 1. A liquid-crystal layer 1 of approximate area 1 cm^2 was placed between two glasses 2. The glasses are coated on the inside by a transparent

0038-5646/77/4605-0999$02.40