SOVIET PHYSICS JETP VOLUME 26, NUMBER 5 MAY, 1968

EFFECT OF UNIAXIAL PRESSURE ON EPR OF Nd^{3+} IN $CaWO_4$ AND THE MAGNITUDE OF SPIN-PHONON INTERACTION IN THE $CaWO_4$:Nd SYSTEM

M. M. ZAITOV and L. Ya. SHEKUN*

Kazan' State University

Submitted May 25, 1967

Zh. Eksp. Teor. Fiz. 53, 1516–1525 (November, 1967)

The EPR line position of Nd^{3+} in a $CaWO_4$ crystal is measured at 4.2°K as a function of the magnitude and direction of external uniaxial pressure. The results obtained yield all components of the spin-phonon coupling tensor G_{ik}, providing complete knowledge of the crystal elasticity is available. Using present (incomplete) knowledge, the G_{ik} and the spin-lattice relaxation times are estimated.

APPLICATION of external pressure to a substance, which changes the spacing and consequently the interaction between its atoms, is accompanied by a change in many of the characteristics of the atoms, in particular, their spectra. Hence, investigation of spectra (optical, EPR, etc.) of crystals subjected to deformation is one of the direct means by which we can find out how an impurity ion interacts with its surroundings and how this interaction depends on the interatomic spacing.[1, 2] The magnitude of this effect will obviously be proportional to the strength of the coupling between the ion and the lattice. In particular, the effect of pressure on EPR will be determined by the magnitude of the spin-phonon interaction (SPI), and so one can find the SPI constants from pressure experiments. To date, the effect of pressure on EPR spectra has been studied for ions of the iron group (see the review[3]). We have observed the effect of uniaxial pressure on the EPR of some rare earth ions in scheelite monocrystals. This paper (see [4]) is concerned with Nd^{3+} in $CaWO_4$.

THEORY

We studied the effect of pressure on tetragonal centers. This is the principal type of rare-earth center in the scheelites.[5] The lowest term $4f^3\ {}^4I_{9/2}$ of an Nd^{3+} ion in a tetragonal center is split into five Kramers doublets. The distance to the nearest excited doublet is about 100 cm^{-1}.[6] Hence only the lowest doublet is populated at the helium temperatures at which EPR is observed. The EPR spectrum consists of one line (we consider only the even isotopes of Nd) and is described by the axial spin Hamiltonian

$$\mathscr{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y), \tag{1}$$

where the z axis coincides with the c axis of the crystal and x and y lie in the ab plane. The Hamiltonian parameters are $g_{\parallel} = 2.03$ and $g_{\perp} = 2.54$.[7]

The application of pressure to the crystal results in adding a perturbation $\mathscr{H}'$ to the Hamiltonian (1), linear in magnetic field, spin, and deformation:[8]

$$\mathscr{H}' = \sum_{iklm} G_{iklm} S_i H_k u_{lm}. \tag{2}$$

Here i, k, l, m = x, y, z; u_{lm} is the deformation tensor.

The tensor G determines the magnitude of the effect. It is symmetric in the second pair of subscripts. A fourth-rank tensor possessing this property has in general 54 different components. The presence of symmetry results in the appearance of relations among the various G_{iklm} that result in the reduction of the number of independent components of the tensor G.

The tetragonal centers in the scheelites have, strictly speaking, the local symmetry S_4 (the experimental demonstration of this fact is contained, for example, in [9]). With S_4 symmetry the tensor G has 27 nonzero components, 14 of which are linearly independent. It is known, however, that in calculations of the effects of the crystalline field in scheelites, one can assume with good approximation that the local symmetry of the centers is D_{2d}.[10, 5] This can be seen by considering the arrangement of the eight oxygens that are nearest to the Nd^{3+} (see Fig. 2). Hence in this paper we shall assume that the local field has symmetry D_{2d}. Then the G tensor has 21 nonzero components. We give these components together with the 13 relations that connect them:

$$\begin{gathered} G_{xxxx} = G_{yyyy}, \quad G_{zzzz}, \\ G_{xxyy} = G_{yyxx}, \quad G_{xxzz} = G_{yyzz}, \quad G_{zzxx} = G_{zzyy}, \\ G_{xyxy} = G_{xyyx} = G_{yxyx} = G_{yxxy}, \\ G_{xzxz} = G_{yzyz} = G_{xzzx} = G_{yzzy}, \\ G_{zxzx} = G_{zyzy} = G_{zxxz} = G_{zyyz}. \end{gathered} \tag{3}$$

Thus, with symmetry D_{2d} the G tensor has eight independent components. For definiteness they can be chosen, for example, as follows: G_{11}, G_{12}, G_{13}, G_{31}, G_{33}, G_{55}, G_{66}, G_{77} with the notation 1 = xx, 2 = yy, 3 = zz, 4 = yz, 5 = xz, 6 = xy, 7 = zx. It is important to note that the simplest form of the Hamiltonian $\mathscr{H}'$ occurs only when x, y, z are the principal directions of the G tensor, when they are associated with the symmetry elements of the immediate surroundings. In deriving the relations (3) we assumed that z was taken along the rotary-reflection axis of fourth order and x and y along the horizontal axes of second order of the symmetry group D_{2d}. These same directions also serve as the principal axes of the crystalline potential.

---

*Deceased.

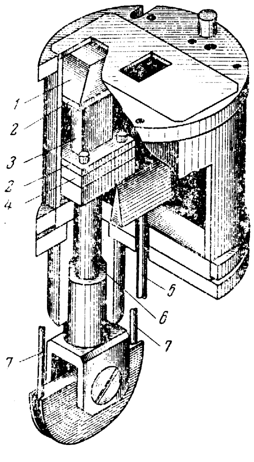


FIG. 1. H_{101} resonator permitting application of pressure perpendicular to the direction of the external magnetic field.

If polar coordinates are used, in which the angles θ and φ are measured from the corresponding principal directions, the Hamiltonian $\mathscr{H}'$ can be written

$$\begin{aligned}\mathscr{H}' = H\{[G_{11}(S_x u_1 \cos\varphi + S_y u_2 \sin\varphi) \\ + G_{12}(S_x u_2 \cos\varphi + S_y u_1 \sin\varphi) + G_{13}(S_x \cos\varphi + S_y \sin\varphi) u_3 \\ + 2G_{55}S_z(u_4 \sin\varphi + u_5 \cos\varphi) + 2G_{66}(S_x \sin\varphi + S_y \cos\varphi) u_6] \sin\theta \\ + [G_{31}S_z(u_1 + u_2) + G_{33}S_z u_3 + 2G_{77}(S_y u_4 + S_x u_5)] \cos\theta\}.\end{aligned} \tag{4}$$

The pressure changes the eigenvalues of the Hamiltonian (1) E_1 and E_2 by quantities ΔE_1 and ΔE_2 that are known to be small. Therefore, in calculating the latter we may limit ourselves to the diagonal matrix elements of

$$\Delta E_1 = \langle\psi_1|\mathscr{H}'|\psi_1\rangle, \quad \Delta E_2 = \langle\psi_2|\mathscr{H}'|\psi_2\rangle. \tag{5}$$

Putting $\Delta E_1 - \Delta E_2 = \Delta(E_1 - E_2) = \Delta(h\nu)$, we obtain for the magnitude of the effect the expression

$$\begin{aligned}\Delta(h\nu) = H\Big\{\frac{g_\perp}{g}[G_{11}(u_1\cos^2\varphi + u_2\sin^2\varphi) + G_{12}(u_1\sin^2\varphi + u_2\cos^2\varphi) \\ + G_{13}u_3 + 2G_{66}u_6\sin 2\varphi]\sin^2\theta + \left(\frac{g_\parallel}{g}G_{55} + \frac{g_\perp}{g}G_{77}\right) \\ \times (u_4\sin\varphi + u_5\cos\varphi)\sin 2\theta + \frac{g_\parallel}{g}[G_{31}(u_1 + u_2) + G_{33}u_3]\cos^2\theta\Big\}.\end{aligned} \tag{6}$$

Having obtained eight relations like (6) from experiment, we can then find all G_{ik}.

Knowing the constants G, we can in principle calculate the probabilities of all relaxation processes. Such calculations were performed by Koloskova[8] and afterwards by Ray.[11] The most interesting probabilities are those of the direct, single-phonon processes. They are quadratic functions of G. The inverse time of the direct processes T_{1d}^{-1} is a linear combination of the probabilities. The formulas for T_{1d}^{-1} for tetragonal symmetry are rather complicated; we therefore give only two special cases:

$$T_{1d}^{-1} = \frac{32\pi k}{3\hbar^2\rho v^5}\nu^2 H^2 T G_{77}^2, \quad H \parallel z; \tag{7}$$

$$\begin{aligned}T_{1d}^{-1} = \frac{32\pi k}{3\hbar^2\rho v^5}\nu^2 H^2 T \Big\{(G_{55}^2 + 16G_{66}^2)(\cos^4\varphi + \sin^4\varphi) \\ + [(G_{11} - G_{12})^2 - 4G_{66}^2]\cos^2\varphi\sin^2\varphi\Big\}, \quad H \perp z.\end{aligned} \tag{8}$$

In these formulas ρ is the density of the crystal, v is the sound velocity, and ν is the microwave resonance frequency.

EXPERIMENT

The method of measuring the EPR line shifts differs little from ordinary spectroscopic measurements and can be carried out in any spectrometer having sufficient magnetic field and frequency stability. In our work we used an X-band video spectrometer (ν = 9.1 GHz) with visual presentation on an oscilloscope of the shift of the resonance line relative to a proton signal. The construction of the resonant cavity is of interest, since the measurements were made at helium temperature.

Most of the measurements were made in an H_{101} rectangular cavity in which the pressure on the sample was applied perpendicular to the direction of the external magnetic field. Its construction is shown in Fig. 1. The sample 3, to which the cardboard cushions 2 are attached, was positioned between a Teflon pedestal 1 and a polystyrene piston 6. Between the piston and the sample there is also a Teflon prism 4. Experiment showed that these fittings on the working faces of the sample sustained the applied forces without damage (in our experiments these forces reached 25 kg), and the remanent elasticity of the Teflon supports at helium temperatures permitted a reduction in the care with which the elements of the pressure system had to be arranged. In any case, we did not notice any shift of the EPR line due to a possible bending of the sample, nor was any broadening of the line as a consequence of inhomogeneously applied pressure observed. The piston 6 takes the force from the struts 7, which are passed around a balancing block and connected to a dynamometer through a free vacuum seal. Support for the whole resonator was provided by a rectangular waveguide transmission line, which had a slightly elliptical cross section to make it more rigid. Ahead of the resonator the waveguide was necked down along its narrow wall to a cross section of 6 × 23 mm. This served to take the load off the thin iris of the resonator. The resonator was tuned by means of the dielectric wedge 5.

The cases in which the pressure was directed along the magnetic field were realized in a cavity of different construction. This was a cylindrical H_{111} cavity. The sample was placed on the side wall of the cavity and received pressure from a Teflon rod that was connected by a thin-walled bellows to a pressure chamber. Helium gas under pressure was introduced into this chamber. In this way the maximum force at a pressure of 20 atm amounted to about 18 kg.

All the investigated samples were in the form of rectangular parallelepipeds, and the pressure was determined by calculating the applied force per unit cross section of the sample. For the usual sections of 5 to 10 mm^2, the pressure was about 500 to 250 kg/cm^2. The forces acting on the lateral surfaces of the samples could be neglected in our experiments, so that we realized the case of so-called "simple compression" ([12], p. 24). In this case the stress tensor σ_{ik} is constant over the entire volume of the sample and is simply related to the pressure P applied to the ends:

$$\sigma_{ik} = P n_i n_k, \tag{9}$$

where **n** is a unit vector in the pressure direction. If the sample is cut along the z axis, σ_{ik} has only one

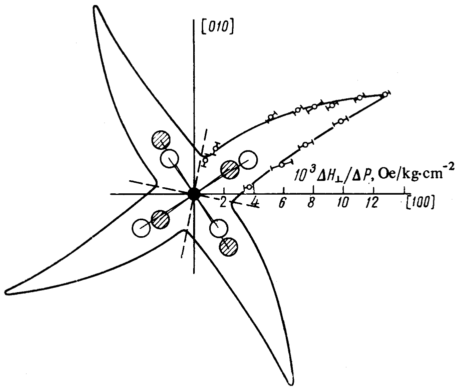


FIG. 2. Azimuthal dependence of $\Delta H/\Delta P$. **H** and **P** are mutually perpendicular and lie in the (001) plane of the $CaWO_4$ crystal. The oxygens surrounding the Nd^{3+} ion are shown in plan view; the shaded ions lie behind the ab plane. The crystal field axes are shown by dashed lines.

component $\sigma_{zz} = P$. By knowing the stress field, it is possible in principle to find the deformations u_{ik}, using Hooke's law for crystalline bodies:

$$u_{ik} = \sum_{lm} s_{iklm}\sigma_{lm}. \tag{10}$$

If we substitute u_{ik} in (6), only the components of G remain unknown. However, before we find them, we must determine the orientation of the principal axes x and y relative to the crystal axes. The structure of scheelite is such that it is impossible to say in advance how the principal axes of the local field are directed. Therefore, we determined the dependence of the quantity $\Delta H/\Delta P$ on the direction of **P**, with **P** and **H** always in the ab plane and 90° apart.[1] The results are given in Fig. 2. The clearly expressed extrema indicate the principal directions. It is seen that these are closely related to the immediate surroundings of the Nd^{3+}. The x axis may be taken either along a maximum or along a minimum of the "rosette." The choice is arbitrary, but the set of constants G_{ik} for one choice will differ from that for the other in the magnitudes of the components G_{11}, G_{12}, and G_{66}. In the figure one can also see an additional asymmetry of the leaves of the rosette with respect to the maxima. The source of this asymmetry is apparently a monotonic change of the elastic properties of the crystal as the angle between **P** and a is increased. Then in the absence of elastic anisotropy one should expect symmetry of the effect approximately relative to the projections of the "neodymium-oxygen" lines. These directions were the ones chosen as the principal directions of the G tensor.

We note the similarity of the azimuthal dependence of the width of the line studied in the case of Nd^{3+} in $CaMoO_4$.[13] The azimuth of the minimum effect is (18 ± 0.5)° with respect to the [100] direction. The azimuth of minimum line width is (15 ± 3)° with respect to the same direction.

Table I.

№	P ∥	H ∥	Measured quantity	$10^{32}\frac{\Delta(h\nu)}{PH}$, $\frac{\text{erg}}{\text{G}}\,\frac{\text{cm}^2}{\text{dyne}}$
1	x	y	$s_{12}G_{11} + s_{11}G_{12} + s_{13}G_{13}$	8.2
2	x	x	$s_{11}G_{11} + s_{12}G_{12} + s_{13}G_{13}$	—11.1
3	z	x	$s_{13}(G_{11} + G_{12}) + s_{33}G_{13}$	0,4
4	z	z	$2s_{13}G_{31} + s_{33}G_{33}$	—5,8
5	x	z	$(s_{11} + s_{12})G_{31} + s_{13}G_{33}$	~0

In order to find all components of the G tensor it is necessary to obtain eight linearly independent combinations. In the course of the measurements we realized the following experimental situations

1) $\mathbf{P} \parallel z, \mathbf{H} \parallel z$; 2) $\mathbf{P} \parallel x, \mathbf{H} \parallel z$;

$$\Delta(h\nu) = H[G_{31}(u_1 + u_2) + G_{33}u_3]; \tag{11}$$

3) $\mathbf{P} \parallel z$, $\mathbf{H} \parallel x$; 4) $\mathbf{P} \parallel x$, $\mathbf{H} \parallel x$;

$$\Delta(h\nu) = H(G_{11}u_1 + G_{12}u_2 + G_{13}u_3); \tag{12}$$

5) $\theta = 90°$, φ arbitrary. The directions of **H** and **P** are mutually perpendicular and lie in the xy plane:

$$\Delta(h\nu) = H[G_{11}(u_1\cos^2\varphi + u_2\sin^2\varphi) + G_{12}(u_1\sin^2\varphi + u_2\cos^2\varphi) + G_{13}u_3 + 2G_{66}u_6\sin 2\varphi]. \tag{13}$$

By giving the angle φ all possible values, it is possible to obtain from (13) an arbitrary number of expressions containing G_{11}, G_{12}, G_{13}, and G_{66}, but only two of them turn out to be linearly independent.

6) $\varphi = 0$, θ arbitrary. **P** lies in the zx plane and is perpendicular to the magnetic field:

$$\Delta(h\nu) = H\left\{\frac{g_\perp}{g}(G_{11}u_1 + G_{12}u_2 + G_{13}u_3)\sin^2\theta + \left(\frac{g_\parallel}{g}G_{55} + \frac{g_\perp}{g}G_{77}\right)u_5\sin 2\theta + \frac{g_\parallel}{g}[G_{31}(u_1 + u_2) + G_{33}u_3]\cos^2\theta\right\}. \tag{14}$$

Since the coefficients of G_{55} and G_{77} are independent of θ, one can determine only the combination $(g_\parallel G_{55} + g_\perp G_{77})$ from experiment.

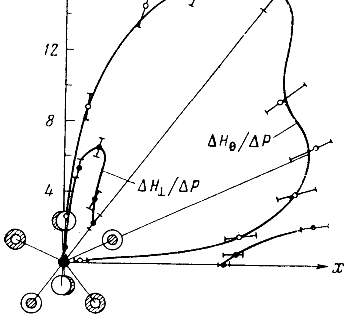
Table I gives the experimental results for simple geometrical situations.

If one takes $\varphi = 45°$ in (13), the effect is proportional to the quantity

$$\tfrac{1}{2}(s_{11} + s_{12})(G_{11} + G_{12}) + s_{13}G_{13} + s_{66}G_{66}$$

and is equal to 2.0 (in the units of Table I). We regard the effect as positive when the resonance field increases, i.e., when $\Delta(h\nu) < 0$.

FIG. 3. Dependence of $\Delta H_\perp/\Delta P$ and $\Delta H_\theta/\Delta P$ on θ. **P** lies in the zx plane and is perpendicular to **H**. $H_\perp$ corresponds to the case $\mathbf{H} \perp z$ and H_θ to an oblique orientation of the magnetic field. In the sketch of the immediate surroundings of the Nd^{3+} ion, the shaded ions (or the shaded parts of them) lie behind the zx plane.



---

[1] Since in all cases we observed a linear dependence of line shift on pressure (see [4]), the experimental results are henceforth given in the form of the values of the quantity $\Delta H/\Delta P$ for corresponding directions of **P** and **H**.

We do not give the cumbersome equation containing G_{55} and G_{77}. It can be obtained from Eq. (14). The corresponding experimental points are shown in Fig. 3.

The experimental results pertaining to the cases **P** ∥ **H** (lines 2 and 4 of Table I) are:

$\mathbf{P} \parallel x,\ \mathbf{H} \parallel x: \quad \Delta H / \Delta P = -12.0 \cdot 10^{-3}$ Oe/kg · cm^{-2}

$\mathbf{P} \parallel z,\ \mathbf{H} \parallel z: \quad \Delta H / \Delta P = -9.9 \cdot 10^{-3}$ Oe/kg · cm^{-2}

ESTIMATION OF THE COMPONENTS OF THE G TENSOR

To this point we have given the experimental results without bringing in any information about the elasticity of the crystal. To evaluate the constants of G it is necessary to expand in terms of the matrix s_{iklm} entering in (10) or its inverse c_{iklm} which also relates the stresses and strains:

$$\sigma_{ik} = \sum_{lm} c_{iklm} u_{lm}.$$

For the scheelite crystal seven constants are non-zero: c_{11}, c_{12}, c_{13}, c_{33}, c_{16}, c_{44}, c_{66}. Only two of these constants are known:[14]

$$c_{33} = 12{,}94 \cdot 10^{11} \text{ dyne/cm}^2 \qquad c_{44} = 3.365 \cdot 10^{11} \text{ dyne/cm}^2$$

and one relation between them:

$$c_{11} - c_{16} \approx c_{12} - c_{66}, \tag{15}$$

so that it does not appear possible to determine G_{ik} exactly. We therefore use the following approach.

By making certain assumptions about the constants c_{ik}, we can complete the matrix c_{ik} and thus obtain s_{ik} and G_{ik}. The set of constants G_{ik} will, of course, rather strongly depend on these assumptions, but in this way we shall at any rate obtain some idea about the orders of magnitude of the G_{ik} and the relations among them. We enumerate the approximations we have used below.

Model 1. We assume elastic isotropy. We take $c_{11} = c_{33} = 12.94$ (here and below all c_{ik} are given in the units 10^{11} dyne/cm^2), $c_{44} = c_{66} = 3.365$, $c_{16} = 0$. From the condition of isotropy $c_{11} = c_{12} = 2c_{44}$, we find $c_{12} = c_{13} = 6.21$. The inverse matrix is $s_{11} = s_{33} = 1.122$ (here and below all s_{ik} are given in the units 10^{-12} cm^2/dyne), $s_{12} = s_{13} = -0.364$, $s_{44} = s_{66} = 2.972$, $s_{16} = 0$. For the calculation we substituted the maximum magnitude of the effect $\Delta(h\nu)/PH = 13.2 \times 10^{-32}$ erg cm^2/G dyne in the first equation of Table I.

Model 2. To the preceding set of c_{ik} we add the elastic contents c_{16}, using (15):

$$c_{16} \approx c_{11} - c_{12} + c_{66} = 10{,}1.$$

In this case a rotation about the z 'axis by about 33° is necessary to transform the inverse matrix to the accepted axes x and y. After this procedure we obtain

$$s_{11} = 0.493;\ s_{12} = 0.676;\ s_{13} = -0.364;\ s_{33} = 1.122;$$
$$s_{44} = 2.972;\ s_{16} = -0.378;\ s_{66} = -1.18.$$

Model 3. We introduce the cubic approximation:

$$c_{11} = c_{33} = 12.94;\ c_{44} = c_{66} = 3.365;\ c_{16} = 0.$$

Assuming fulfillment of the Cauchy condition $c_{12} = c_{44}$, we find $c_{12} = c_{13} = 3.365$. After rotation of the inverse matrix, we have

$$s_{11} = 1.052;\ s_{12} = -0.364;\ s_{13} = -0{,}179;\ s_{33} = 0{,}866;$$
$$s_{44} = 2{,}972;\ s_{16} = 0.162;\ s_{66} = 2{,}230.$$

Model 4. To the preceding matrix of the elastic constants we add c_{16} from condition (15). Then

$$s_{11} = 0.425;\ s_{12} = 0.576;\ s_{13} = -0{,}179;\ s_{33} = 0{,}866;$$
$$s_{44} = 2.972;\ s_{16} = -0{,}308;\ s_{66} = -0.866.$$

Model 5. The lattice of zircon $ZrSiO_4$ is similar in structure to that of scheelite. The elastic constants of zircon are known.[15] Since the crystallographic axes of zircon pass through the oxygen ions, then for a better similarity it is necessary to rotate the matrix of the elastic constants of zircon by an angle of 33° about the z axis. Assuming that for similar lattices there exists a proportionality of the elasticity constants, we can find the matrix of elasticity for scheelite in the "zircon approximation:"

$$\|c_{ik}\|_{CaWO_4} = 2{,}624\ \|c_{ik}\|_{ZrSiO_4},$$

where 2.624 is the average value of the ratios of the constants c_{33} and c_{44}. The constant c_{16} is introduced according to the condition (15). The inverse matrix after rotation of 33° about the z axis has the following elements:

$$s_{11} = 0{,}315;\ s_{12} = 0{,}501;\ s_{13} = 0{,}046;\ s_{33} = 0{,}783;$$
$$s_{44} = 2.972;\ s_{16} = -0{,}382;\ s_{66} = -1{,}120.$$

The results of the calculations of the components of the G tensor on the basis of all these models are presented in Table II.

DISCUSSION

First we compare the magnitude of the effect for Nd^{3+} in $CaWO_4$ and for the iron-group ion $3d^7$ Co^{2+} in MgO.[16] A convenient quantity for the comparison is the relative change of the g factor $\delta g/g$ for the same pressure. In [16] the values of δg for a pressure of 6.34×10^8 dyne/cm^2 are given. The maximum δg is 0.020, corresponding to $\delta g/g = 4.7 \times 10^{-3}$. For Nd^{3+} in $CaWO_4$ in the orientation **H** ∥ x, **P** ∥ x for the same pressure we have $\delta g/g = 3 \times 10^{-3}$. In an intermediate orientation $\delta g/g$ increases approximately to $(4-4.5) \times 10^{-3}$. Thus, the relative magnitude of the effect for Nd^{3+} in $CaWO_4$ does not exceed that for Co^{2+} in MgO.

Under compression of the crystal along the c(z) axis, the unit cell is compressed, and the change in its length c can be evaluated from the relations

$$\Delta c = c u_{zz} = c s_{33} \sigma_{zz} = c s_{33} P.$$

from the results presented in the preceding section it is seen that the constant s_{33} depends weakly on the model taken and equals $(0.9-1.1) \times 10^{-12}$ cm^2/dyne. Taking $s_{33} = 10^{-12}$ cm^2/dyne and assuming a concrete pressure, say P = 100 kg/cm^2, we obtain $\Delta c/c = -10^{-4}$,

Table II.

Model	$G_{ik} \cdot 10^{20}$, erg/G						
	G_{11}	G_{12}	G_{13}	G_{31}	G_{33}	G_{44}	$g_{\parallel} G_{55} + g_{\perp} G_{77}$
1	—6,0	10.5	1.8	—1,9	—4,0	0,33	32,6
2	51,2	—54.0	—0,6	—1,0	—4,6	—2,9	31,9
3	—9,0	4,6	—0,5	—1,6	—6,1	1,6	31,6
4	62,3	—65,2	—0,2	—1,1	—6,3	—4,0	32,0
5	50,0	—53,6	0,7	0,42	—7,5	—3,7	32,3

corresponding to $\Delta c \approx -0.0012$ Å. At the same time $\Delta g_{\parallel} = -6.3 \times 10^{-4}$ and $\Delta g_{\perp} = +0.4 \times 10^{-4}$. A change in c also occurs in moving through the homologous scheelite series, whereby $g_{\parallel}$ varies linearly with a change in c.[17] From the graph in [17] we find that a change $\Delta c/c = 10^{-4}$ corresponds to $\Delta g_{\parallel} = 10^{-3}$, $\Delta g_{\perp} = -0.8 \times 10^{-4}$. It is curious that the shifts in the g factors due to pressure and due to change in host-lattice are so close in magnitude.

Finally, we estimate the spin-lattice relaxation time. Since the dispersion of G is so great, we shall calculate those maximum and minimum values of T_{1d} yielded by the sets in Table II. For $|G_{77}|$ we take the values $(2-15) \times 10^{-20}$ erg/G. From [14] we choose $\rho = 6.12$ g/cm³ and calculate $\langle v^5 \rangle = 1.04 \times 10^{27}$ cm⁵/sec⁵. The results of calculations from formulas (7) and (8) are

$$T_{1d}^{-1} = (2.6 - 18.5) \cdot 10^{-28} \nu^2 H^2 T, \quad H \parallel z;$$
$$T_{1d}^{-1} = (186 - 400) \cdot 10^{-28} \nu^2 H^2 T, \quad H \perp z, \quad \varphi = 0.$$

Substituting $\nu = 9.4$ GHz and H = 3300 Oe (the same frequency at which the relaxation time of Nd^{3+} in scheelites was measured in [18]), we obtain

$$T_{1d} = T^{-1}\ (0.06 - 4.0)\ \text{sec} \cdot \text{deg}, \ H \parallel z. \tag{16}$$

For $H \perp z$ ($\nu = 9.4$ GHz, H = 2650 Oe), we find

$$T_{1d} = T^{-1}\ (0.02 - 0.05)\ \text{sec} \cdot \text{deg}. \tag{17}$$

Let us compare these numbers with the results of measurements of T_{1d} by the pulse saturation method. It should be emphasized that it makes sense to compare the experimental times with theory only when it is certain that the condition

$$T_{1d}^{-1} \sim \nu^2 H^2 T \tag{18}$$

is fulfilled, which is far from being a frequent occurrence. From [18] and [19] it comes out that at 9.4 GHz direct processes dominate in the $CaWO_4$:Nd system in the temperature interval 1.5° to 2.5°K. The samples of $CaWO_4$ with 0.01% Nd investigated in [19] gave times obeying the law (18), and therefore there is a basis for assuming that in this case the true time for the direct process was measured. We can find from the graphs in [19] that at T = 2°K and $\nu = 9.4$ GHz,

$$\begin{gathered} T_{1d} \approx 0.4\ \text{sec},\ H \parallel z, \\ T_{1d} \approx 1.5\ \text{sec},\ H \perp z. \end{gathered} \tag{19}$$

Formulas (16) and (17) give

$$\begin{gathered} T_{1d} = (0.03 \div 2.0)\ \text{sec}.\ H \parallel z; \\ T_{1d} = (0.01 \div 0.025)\ \text{sec}.\ H \perp z. \end{gathered} \tag{20}$$

Thus the times calculated from the results of the pressure experiments are on the average one to two orders shorter than the times measured by the pulse method. In addition, the angular dependence of T_1 is not even qualitatively reproduced. Nevertheless, the agreement between the quantities in (19) and (20) is a great deal better than for T_1 of the Co^{2+} ion in MgO, where the pressure experiments yield times four orders longer than those obtained from pulse measurements.[16]

One of the sources for the discrepancies between (19) and (20) may be the incompleteness of our knowledge about the elasticity of $CaWO_4$ and consequently the inaccuracy of the numbers G_{ik}. If this is so, then the character of the discrepancies ought to be maintained for other rare earth ions in $CaWO_4$ as well. An important contribution to these discrepancies may be due to a local change in the elastic properties of the crystal lattice at the sites where the impurity ions are located.

The experimental material concerning the effect of pressure on the EPR of Kramers doublets is still very scanty. Hence it must be asserted that in order to understand the sources of the strong divergences that appear in estimates of spin-phonon coupling, it is absolutely necessary to have new pressure experiments, particularly on crystals whose elastic properties are well known.

We consider it our pleasant duty to thank S. A. Al'tshuler, B. I. Kochelaev, B. Z. Malkin, and L. K. Aminov for their interest in our work and for helpful discussions. We are indebted to A. I. Smirnov for the gift of a $CaWO_4$ sample, V. M. Vinokurov and G. A. Krinari for x-ray orientation of the samples, N. G. Koloskova for assistance in the calculation of the relaxation times, and O. I. Mar'yakhina for carrying out a number of calculations.

---

[1] W. M. Walsh and N. Bloembergen, Phys. Rev. **107**, 904 (1957).

[2] A. A. Kaplyanskiĭ, Opt. Spektrosk. **7**, 677 (1959) [Opt. Spectrosc. **7**, 406 (1959)].

[3] E. B. Tucker, Proc. IEEE **53**, 1547 (1965).

[4] M. M. Zaitov and L. Ya. Shekun, ZhETF Pis. Red. **4**, 338 (1966) [JETP Lett. **4**, 228 (1966)].

[5] L. Ya. Shekun, Opt. Spektrosk. **22**, 776 (1967).

[6] Ya. É. Kariss, A. M. Morozov, and P. P. Feofilov, Opt. Spektrosk. **17**, 887 (1964) [Opt. Spectrosc. **17**, 481 (1964)].

[7] N. E. Kask, L. S. Kornienko, A. M. Prokhorov, and M. Fakir, Fiz. Tverd. Tela **5**, 2303 (1963) [Sov. Phys.-Solid State **5**, 1675 (1963-4)].

[8] N. G. Koloskova, Paramagnitnyĭ rezonans (Paramagnetic Resonance) Kazan University Press, 1964, p. 115.

[9] W. B. Mims, Phys. Rev. **140**, A531 (1965).

[10] L. Ya. Shekun, Fiz. Tverd. Tela **8**, 1717 (1966) [Sov. Phys.-Solid State **8**, 1370 (1966)].

[11] D. K. Ray, T. Ray, and P. Rudra, Proc. Phys. Soc. (London) **87**, 485 (1966).

[12] L. D. Landau and E. M. Lifshitz, Teoriya uprugosti (Theory of Elasticity), Fizmatgiz, 1965 [Addison-Wesley 1959].

[13] I. N. Kurkin and L. Ya. Shekun, Fiz. Tverd. Tela **9**, 444 (1967) [Sov. Phys.-Solid State **9**, 339 (1967)].

[14] D. Gerlich, Phys. Letters **12**, 314 (1964).

[15] K. S. Aleksandrov and T. V. Ryzhova, Kristallografiya **6**, 289 (1961) [Sov. Phys.-Crystallography **6**, 228 (1961)].

[16] E. B. Tucker, Phys. Rev. **143**, 264 (1966).

[17] I. N. Kurkin, Fiz. Tverd. Tela **8**, 731 (1966) [Sov. Phys.-Solid State **8**, 585 (1966)].

[18] A. A. Antipin, A. N. Katyshev, I. N. Kurkin, and L. Ya. Shekun, Fiz. Tverd. Tela **9**, 813 (1967) [Sov. Phys.-Solid State **9**, 636 (1967)].

[19] N. E. Kask, Fiz. Tverd. Tela **8**, 1129 (1966) [Sov. Phys.-Solid State **8**, 900 (1966)].

Translated by L. M. Matarrese
174