Anisotropic spin-lattice relaxation of self-trapped holes in KBr

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The spin-lattice relaxation times τ of self-trapped holes (V_k centers) in KBr containing less than 10^6 F centers and V_k centers per cm^3 are measured using a sensitive luminescence method at temperatures 0.4 and 0.6 K in a magnetic field from 7 to 15 kG. Single-phonon relaxation of the V_k centers is described by the dependence $\tau^{-1} = (AH^3 BH^5)\coth(g\mu H/2kT)$. The term AH^3, which describes the spin-spin relaxation due to the modulation of the isotropic hyperfine interaction, is independent of the orientation of the axis of the V_k center relative to the magnetic field, while the term BH^5, which corresponds to Kronig–Van Vleck mechanism of spin-lattice relaxation, depends on that orientation and, in the case $\mathbf{V}_k \perp \mathbf{H}$, it also depends on the orientation of the crystal. The anisotropy of the spin-lattice relaxation rate is explained by a model of the V_k center which consists of a Br_2^- molecule and the two nearest cations.

INTRODUCTION

Holes in alkali halide crystals can become self-trapped in the form of so-called V_k centers, whose cores consist of $(\text{halogen})_2^-$ diatomic paramagnetic molecules which occupy two adjacent sites along the ⟨110⟩ direction in the face-centered cubic lattice.[1] Investigation of the spin lattice relaxation of V_k centers is of interest because, in contrast to the paramagnetic ions that have been thoroughly studied (see e.g., Ref. 2), in the excited state of the V_k center the spin is coupled to the axis of the molecule. As a result of this coupling, the spin-lattice relaxation rate should depend on the direction of the magnetic field in a characteristic way. In addition, the anisotropy of the spin-lattice relaxation rate gives information, presently lacking for not fully symmetric oscillations, on the magnitude of the electron-vibrational interaction in the V_k center.

To the present time the spin-lattice relaxation of V_k centers has been studied mainly by the paramagnetic resonance saturation method.[3–5] Single-phonon spin-lattice relaxation due to the hyperfine interaction has been studied in Refs. 4 and 5. However, neither the absolute value nor the character of the anisotropy of the measured spin-lattice relaxation rate agreed with the theory for isolated V_k centers.[5] To explain this discrepancy, the so-called fast-relaxation centers were invoked, these centers being formed in the crystal both as a result of the high concentration of F centers and V_k centers ($\sim 10^{18}$ cm^{-3}), and as a result of the introduction of impurities for the purpose of good coloring ability. Thus, the basic mechanisms and the rate of spin-lattice relaxation of self-trapped holes have not as yet been determined.

In this investigation we have used a luminescence method[6–9] to measure the spin-lattice relaxation of V_k centers in a crystal having a low concentration ($< 10^{16}$ cm^{-3}) of centers. The measurement method we used is based on the dependence of the intensity I of the photostimulated recombination luminescence on the spin polarization P of the ground state of the electron F centers and hole V_k centers. The intensity of the singlet-singlet luminescence of $V_k e$ centers (of $(\text{halogen})_2^{2-}$ molecules), formed by the tunneling of an electron to the self-trapped hole, under constant illumination in the F-center absorption band, depends on the temperature T and the magnetic field H like[6]

$$I(H, T) = \beta[1 - \alpha P_F(H, T) P_V(H, T)], \tag{1}$$

where the coefficient β is equal to the intensity of the luminescence in zero field and $\alpha \lesssim 1$ is a factor that takes into account the loss of spin memory after optical excitation of the F center. If a nonequilibrium spin polarization is created by a rapid change in the temperature, the polarization begins to relax towards the equilibrium value

$$P_i = \mathrm{th}(g_i \mu H/2kT), \tag{2}$$

where $g_i\,\mu H$ is the splitting of the spin sublevels. The time dependence of the luminescence intensity (at athe new temperature) is determined by the spin-lattice relaxation rates of the F centers and V_k centers. To study the magnetic field dependence of the spin-lattice relaxation, it is advantageous to forgo the radio-frequency method of exciting the spin system. However, in this case one measures the relaxation rate averaged over the components of the hyperfine structure.

METHOD

For the experimental sample we chose the crystal KBr, which emits intense luminescence in the band of the singlet-singlet transition of the $V_k e$ center. The KBr single crystals were grown in air from a specially pure grade of salt by the Kyropoulos procedure. Plates of dimensions $8 \times 8 \times 3$ mm were fastened into a magnetooptical He^3 cryostat[10] in the center of a superconducting solenoid having a vertical axis, so that the field was parallel either to the ⟨100⟩ or the ⟨110⟩ axis of the crystal with an accuracy better than 3°. The color centers were created by x-irradiation at 80 K. Preferential orientation of the V_k centers was established by irradiation with linearly polarized light in the absorption band of the V_k centers ($\sim$380 nm). The direction of the light polarization vector was chosen such that the centers were oriented either parallel or perpendicular to the magnetic field. The necessary irradiation dose was determined from the saturation value, 20%, of the linear polarization of the recombination luminescence. The concentration of F centers and V_k centers remaining after the orientation was in the range 10^{15}

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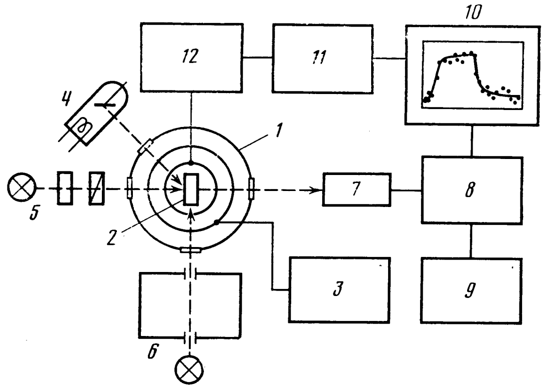

FIG. 1. Experimental diagram of the apparatus. 1) Cryostat, 2) crystal, 3) current source for the superconducting solenoid, 4) x-ray source, 5) lamp, filters (S3S-22-FS-1 + FS-6), and polarizer for orienting the V_k centers, 6) lamp and monochromator for stimulation, 7) filters (UFS-2 and 2 cm saturated solution of $NiSO_4$) and photomultiplier, 8) amplifier/discriminator, 9) pulse counter, 10) multichannel analyzer, 11) computer, 12) heating-current source.

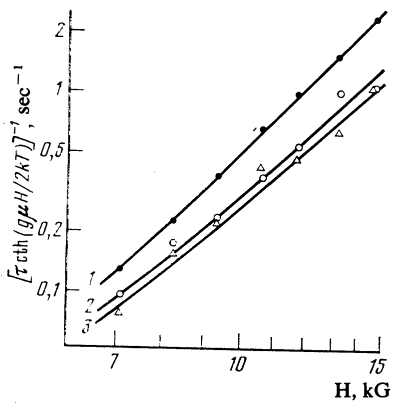

FIG. 2. Spin-lattice relaxation rate as a function of magnetic field for: 1) **H**||**y**, 2) **H**||**z**, 3) **H**||**x**. Curves 1, 2, and 3 are plotted from the formula $[\tau \coth(g\mu H/2kT)]^{-1} = AH^3 + BH^5$. The values of A and B are shown in Table I.

to 10^{16} cm^{-3}. The luminescence in the singlet-singlet band and the stimulation in the F absorption band were measured in directions perpendicular to the magnetic field (see Fig. 1) through a slit in the solenoid. The intensity of the stimulating radiation was held at 10^{11} photons/sec in order to decrease the rate of decay of luminescence intensity due to the decrease in the number of recombining centers (one F center–V_k center pair is annihilated in the emission of one luminescence photon). The intensity of the stimulated luminescence was two orders of magnitude greater than the intensity of the tunneling recombination luminescence occurring without stimulation.

The spin polarization was driven out of equilibrium by a periodic modulation of the temperature of the crystal between 0.4 and 0.6 K produced with a heater attached to the crystal holder. In a special experiment, in which the temperature of the crystal was measured from the resistance of a grafoyl film applied to the crystal, it was shown that the temperature variation was approximately exponential, with a time constant 0.15 sec. The luminescence was measured by a photo-multiplier operated in the photon counting mode. The signal was accumulated for 5 min in a multichannel analyzer synchronized with the heater (10^4 single-photon pulses in each of the 255 channels).

The time dependence of the luminescence intensity, corresponding to heating or cooling was approximated, using least squares, by a two-component exponential:

$$I(t)=I_0+I_1\exp(-t/\tau_1)+I_2\exp(-t/\tau_2). \qquad (3)$$

In the measurements on KBr we found that $\tau_2 \gtrsim 20\tau_1$ and $I_1 \approx I_2$. It is easy to show that if the spin polarizations of the F and V_k centers vary exponentially with greatly differing relaxation rates, then the luminescence intensity (1) is described by formula (3). The value of τ_2 we obtained were in good agreement with previous measurements of the spin-lattice relaxation times of F centers.[11] Consequently, τ_1 describes the spin relaxation of the V_k centers.

At each of the values of the magnetic field the measurements were carried out for several temperature modulation frequencies. In approximating the time dependences, a linear correction was introduced into the total luminescence decay, and an exponential correction was applied to the rate of change of the crystal temperature.

RESULTS

Figure 2 shows log-log plots of the spin-lattice relaxation rate of the V_k centers vs the magnetic field strength for the orientations **H**||**x**, **H**||**y**, and **H**||**z** (see Fig. 3). The relaxation rate is maximal if the magnetic field is along the y axis and minimal if the field is along the x axis. In both cases the axis of the Br_2^- molecule is perpendicular to the magnetic field. In the lengthwise orientation (**H**||**z**) the rate has an intermediate value. The points on the graph were obtained by averaging the experimental data obtained at 0.4 and 0.6 K taking into account that for single-phonon spin-lattice relaxation, $\tau^{-1} \sim \coth(g\mu H/2kT)$. On the basis of physical considerations, these dependences were approximated by least squares by the formula[12]

$$[\tau\,\mathrm{cth}(g\mu H/2kT)]^{-1}=AH^3+BH^5. \qquad (4)$$

The values of A and B that were obtained are shown in Table I. It can be seen that A is isotropic and B is anisotropic. To ascertain the extent to which the measured values of the relaxation rate are characteristic of isolated V_k centers, the measurements were carried out over widely varying stages of

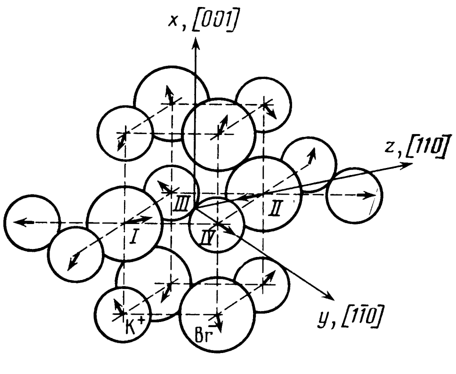

FIG. 3. Cluster in a KBr crystal. This cluster, after capture of a hole and static displacement of the ions as indicated by the arrows, can be taken for a V_k center.

TABLE I. Spin-lattice relaxation constants $B\,[10^6\ \mathrm{sec}^{-1}\cdot\mathrm{kG}^{-5}]$ and $A\,[10^4\ \mathrm{sec}^{-1}\cdot\mathrm{kG}^{-3}]$ and the dimensionless constants h_m^2 for V_k centers in KBr. The error is assumed equal to the double standard deviation.

	Experiment		Theory				
	B	A	A^c	A^d	h_1^2	h_2^2	h_3^2
H‖**x**	0,57±0,25	2.1±0,4	1,11	0,24	0,49	2,47	0
H‖**y**	2,52±0,24	2,5±0,4	1,11	0,096	0,49	0	2,65
H‖**z**	0,77±0.32	2.3±0,4	1,11	0,096	0	0,89	1,12

de-excitation corresponding to an order-of-magnitude change in the concentration of V_k centers and with stimulation in the F' center absorption band. To the limits of experimental error we observed no changes in the relaxation rate of the V_k centers.

DISCUSSION

1. V_k-center model. When a hole is self-trapped, there is a strong local static lattice distortion. Anions I and II come closer together along the **z** axis (by 37% in KBr),[13] the neighboring ions lying in the $z = 0$ plane are repelled, and so forth (see Fig. 3).[14] The local symmetry of the defect is D_{2h}. The EPR spectra of the V_k centers are well described by a model in which the electron wave functions are localized on anions I and II and the effect of the surroundings is described within the crystal field approximation (see Ref. 15, from which we also have taken the numerical characteristics of the V_k center, as cited below). Henceforth we shall use this model.

The ground state of a V_k center,

$$\ldots(a_g)^2(b_{3u})^2(b_{2u})^2(b_{2g})^2(b_{3g})^2(b_{1u}),\qquad |B_{1u}\uparrow,\ \downarrow\rangle,\tag{5}$$

where b_{1u}, b_{2u} and b_{3u} transform as the coordinates **z**, **y**, and **x**, is a Kramers doublet. The arrows ↑ and ↓ designate the spin states, which are quantized along the external magnetic field. In the zero-order approximation the excited states are obtained by the transition of one electron to the unoccupied b_{1u} orbital. The splitting $\delta E = E(B_{2u}) - E(B_{1u}) \approx E(B_{3u}) - E(B_{1u}) \approx 2$ eV is due to the molecular field ($\Sigma - \pi$ splitting). The splitting of the excited states, due to the crystal field, $\Delta = \langle b_{3u}|H_V|b_{3u}\rangle - \langle b_{2u}|H_V|b_{2u}\rangle$, is of the order 0.1 eV and is comparable with the energy λ of the spin-orbit interaction. For example, in KBr $\lambda/\Delta = 36$ while in LiCl $\lambda/\Delta = 0.1$. In the calculations we used basis functions based on the molecular orbitals and diagonalized with respect to these two interactions

$$|\pi_{2u}{}^{\pm}\rangle = u_1|b_{3u}{}^{\pm}\rangle \pm iu_2|b_{2u}{}^{\pm}\rangle,\qquad |\pi_{1u}{}^{\pm}\rangle = u_2|b_{3u}{}^{\pm}\rangle \mp iu_1|b_{2u}{}^{\pm}\rangle,\tag{6}$$

where

$$u_1 = \{0{,}5[1+\Delta(\Delta^2+\lambda^2)^{-1/2}]\}^{1/2},\quad u_2 = \{0{,}5[1-\Delta(\Delta^2+\lambda^2)^{-1/2}]\}^{1/2},$$
$$\lambda = \pm 2i\langle b_{3u}{}^{\pm}|H_{so}|b_{2u}{}^{\pm}\rangle.$$

Here ± indicates the spin states quantized along the axis of the molecule.

2. Spin-lattice relaxation mechanism of the V_k centers. The singlet-phonon spin-lattice relaxation rate can be written in the form of a sum, each term of which gives the spin-lattice relaxation rate determined by the normal vibrations of a single symmetry

$$\tau^{-1} = (g^3\mu^3/8\pi^2\hbar^4\rho)H^3\,\mathrm{cth}(g\mu H/2kT)\times\sum_b\sum_{i\geqslant j}\langle\downarrow|O_i^b|\uparrow\rangle\langle\uparrow|O_j^{b*}|\downarrow\rangle\times\sum_\beta v_\beta^{-5}\int G_i^{\beta b}(\Omega)G_j^{\beta b}(\Omega)\,d\Omega,\tag{7}$$

where

$$G_i^{\beta b}(\Omega) = \sum_{n,m,\alpha}\varepsilon_{i\alpha}{}^b(n,m)\lambda_\alpha{}^\beta q^{-1}\mathbf{R}(n,m)\mathbf{q}.$$

Here $\varepsilon_{i\alpha}^b(n,m)$ is the coefficient of expansion of the coordinate Q_i^b of the ith normal vibration which transforms as the b th irreducible representation of the symmetry group of the defect, in terms of a translation of the mth atom of the nth unit cell in the direction α ($\alpha = x, y, z$). the quantity $\mathbf{R}(n, m)$ is the equilibrium coordinate of n, m atom; $\mathbf{q}$ is the phonon wave vector, λ_α^β are the direction cosines of the phonon polarization vectors; β ($\beta = l, t_1, t_2$) is an index that distinguishes the longitudinal and transverse vibrations; v_β is the speed of sound; ρ is the crystal density; the integration is over the solid angle. The derivation of formula (7) is analogous to that of formula (5.35) of Ref. 2 except that in (7) we do not neglect vibrations that rotate the defect.[16,17] The terms of the operator

$$O_i^b = \frac{\partial V}{\partial Q_i^b} + \frac{\partial a_c}{\partial Q_i^b}\mathbf{IS},\tag{8}$$

that effect the dynamic coupling between the electron spin system and the lattice vibrations via the modulation of the electric field V and of the hyperfine contact interaction a_c govern the spin-lattice relaxation mechanisms. The spin-lattice relaxation rate depends on the magnetic field like

$$\tau^{-1} = (A^c + A^d + BH^2)H^3\,\mathrm{cth}(g\mu H/2kT),\tag{9}$$

where A^c and A^d describe the relaxation via the hyperfine interaction and B describes the Kronig–Van Vleck spin-lattice relaxation mechanism. The spin-lattice relaxation mechanisms associated with the hyperfine interaction have been investigated in Ref. 5, and we use those results below for the KBr crystal.

According to Ref. 13, the hyperfine contact interaction constant depends on the internuclear spacing r of the $(\mathrm{halogen})_2^-$ quasimolecule in the following way:

$$a_c(r) = a_0 + a_1\exp[-(r-r_0)/a^*].\tag{10}$$

Taking into account only the contribution from the totally symmetric vibrations, we obtain for the operator O_i^b

$$O_i^b = -2^{1/2}(a_1/a^*)\mathbf{IS}.\tag{11}$$

Here $\mathbf{I} = \mathbf{I}_1 + \mathbf{I}_2$, where $\mathbf{I}_i$ is the spin operator of the ith nucleus. Substituting (11) into (7) we obtain the formula for A^c

$$A^c=0{,}2546\overline{\langle\downarrow|\mathbf{IS}|\uparrow\rangle^2}(\mu^3a_1{}^2r_0{}^2/\hbar^4\rho a^{*2})\,({}^1/{}_3v_{t_1}{}^{-5}+{}^1/{}_3v_{t_2}{}^{-5}+v_l{}^{-5}),\tag{12}$$

where the bar over the matrix element means an average over all the values of the total spin angular momentum of the nucleus and of its projection in the direction of the magnetic field.

The electric field operator does not contain the spin operator and the orbital angular momentum of the ground state is zero. To obtain a nonzero transition probability between the components of the Kramers doublet as a result of the modulation of the electric field it is necessary to take into account the admixture of the excited states (6) in the ground state (5) in two ways: a) through the anisotropic hyperfine interaction operator $\Sigma_{\alpha>\beta}\, D_{\alpha\beta}\, I_\alpha\, S_\beta$ (Ref. 5); this mechanism determines A^d in Eq. (9), and b) through the spin-orbit and Zeeman interaction operators (the Kronig–Van Vleck mechanism). For the Kronig–Van Vleck mechanism we obtain from (7) in second order perturbation theory

$$\begin{aligned}B=[g^3\mu^5\lambda'^2/8\pi^2\hbar^4\rho(\delta E)^4]\Big\{&h_b{}^2(\mathbf{H}/H,\lambda,\Delta)\\&\times\sum_{i\geqslant j}\langle B_{au}|\frac{\partial V}{\partial Q_i{}^b}|B_{cu}\rangle\langle B_{cu}|\frac{\partial V}{\partial Q_j{}^b}|B_{au}\rangle\\&\times\sum_\beta v_\beta{}^{-5}\int G_i{}^{\beta b}(\Omega)\,G_j{}^{\beta b}(\Omega)\,d\Omega\\&+\mathrm{perm}(a,b,\mathrm{c})\Big\},\end{aligned}\tag{13}$$

where the remaining two terms in the curly brackets are obtained from the first by cyclic permutation of the indices $a, b, c = 1, 2$, and 3. The non-totally-symmetric vibrations of symmetry β_{1g}, β_{2g}, and β_{3g} contribute to the relaxation. The dependence of B on the orientation is included in the dimensionless coefficients h_b. The expressions for h_b for an arbitrary direction are complicated. Here we show these expressions for the three field orientations that we used.

for $\mathbf{H}\|\mathbf{z}$ (14)

$$h_3=2+(\Delta^2-\lambda^2-2\Delta\lambda)/(\Delta^2+\lambda^2),$$

$$h_2=2+(\Delta^2-\lambda^2+2\Delta\lambda)/(\Delta^2+\lambda^2),\quad h_1=0;$$

for $\mathbf{H}\|\mathbf{y}$

$$h_3=1+\delta\lambda/\delta_z\lambda'-(\Delta^2+\Delta\lambda)/(\Delta^2+\lambda^2),$$

$$h_2=0,\quad h_1=\delta;$$

for $\mathbf{H}\|\mathbf{x}$

$$h_3=0,\quad h_2=1+\delta\lambda/\delta_z\lambda'-(\Delta^2-\Delta\lambda)/(\Delta^2+\lambda^2),$$

$$h_1=\delta.$$

Here $\delta=i\langle b_{2u}|l_x|b_{1u}\rangle\approx i\langle b_{1u}|l_y|b_{3u}\rangle$,

$$\delta_z=i\langle b_{3u}|l_z|b_{2u}\rangle,\ \lambda'=2i\langle b_{2u}{}^{\mp}|H_{so}|b_{1u}{}^{\pm}\rangle$$

$$\approx\pm2\langle b_{1u}{}^{\mp}|H_{so}|b_{3u}{}^{\pm}\rangle,$$

where l_α is the orbital angular momentum operator. From (14) it can be seen that the anisotropy of the Kronig–Van Vleck mechanism is determined, first, by the character of the interaction with the non-totally-symmetric vibrations (for each vibration there is one direction of the magnetic field for which it is inactive), and second, by the properties of the diatomic molecule (h_2 and h_3 depend essentially on λ/Δ).

3. Discussion of experimental and theoretical results. The numerical values of the coefficients h_b^2 for KBr are given in Table I ($\Delta = -0.007$ eV, $\lambda = 0.25$ eV, $\lambda' = 0.29$ eV, $\delta = 0.7$, and $\delta_z = 1$). The experimentally determined anisotropy of the spin-lattice relaxation rate can be qualitatively understood if we postulate that the self-trapped hole interacts only with the non-totally-symmetric vibrations β_{3g}. Actually, in the two cases where the axis of the molecule is perpendicular to the magnetic field (see Fig. 3) the experiment gives $B(\mathbf{H}\|\mathbf{y}) > B(\mathbf{H}\|\mathbf{x})$. In the two cases where the magnetic field is along the ⟨110⟩ axis but is either parallel or perpendicular to the axis of the molecule, we have $B(\mathbf{H}\|\mathbf{y}) > B(\mathbf{H}\|\mathbf{z})$. These same relations between the corresponding coefficients h_b^2 are satisfied for β_{3g} vibrations and are not satisfied for β_{2g} or β_{1g} vibrations (see Table I).

The simplest model of a V_k center which has all the vibrations present in the spin-lattice relaxation is a planar four-ion complex (anions I and II and cations III and IV in Fig. 3) in a crystal. Three librational symmetry vibrations β_{1g}, β_{2g}, and β_{3g} correspond to rotations of the entire complex about the **z**, **x**, and **y** axes. The single "internal" vibration (in which the two ion pairs I, II and III, IV vibrate around the **x** axis in antiphase) has β_{3g} symmetry. It is natural to suppose that it is this latter vibration that is characterized by the largest electron-phonon interaction constant.

To evaluate the electron-phonon interaction constant, we write down formula (13) in the form of three equations linear in the squares of the matrix elements, where, in the place of B, we use its three experimental values for the three orientations of the field (we have neglected the librational β_{3g} vibration in comparison to the internal one). We obtain

$$\begin{aligned}&\Big|\langle B_{2u}|\frac{\partial V}{\partial Q^3}|B_{1u}\rangle\Big|=0.25\pm0{,}04\ \ \mathrm{eV}\cdot\text{Å}^{-1},\\&\Big|\langle B_{3u}|\frac{\partial V}{\partial Q^1}|B_{2u}\rangle\Big|=0.35\pm0{,}18\ \ \mathrm{eV}\cdot\text{Å}^{-1},\\&\Big|\langle B_{1u}|\frac{\partial V}{\partial Q^2}|B_{3u}\rangle\Big|<0{,}20\ \ \mathrm{eV}\cdot\text{Å}^{-1},\end{aligned}\tag{15}$$

where we have used $v_l = 2.97\cdot10^5$ cm/sec, $v_{t_1} = 2.22\cdot10^5$ cm/sec, $v_{t_2} = 1.35\cdot10^5$ cm/sec, $R_0 = 6.596$ Å for the lattice constant,[18] $\rho = 2.75$ g/cm^3, and $\delta E = 2.19$ eV.

The values of the electron-phonon interactions are acceptable, since the differences of the matrix elements of the interaction operator corresponding to the totally symmetric vibrations are of the order 3 eV/Å (this estimate can be made on the basis of the results of Ref. 19). On the other hand, by regarding the β_{2g} and β_{3g} vibrations as librations of the (halogen)$_2^-$ diatomic molecule about the **y** and **x** axes we obtain in the adiabatic approximation an estimate for the electron-phonon interaction constant that in order of magnitude agrees with (15) (Ref. 5).

$$\langle B_{2u}|\frac{\partial V}{\partial Q^3}|B_{1u}\rangle\approx\langle B_{1u}|\frac{\partial V}{\partial Q^2}|B_{3u}\rangle$$

$$\approx-2^{1/2}\delta E/R_0=-0{,}47\ \ \mathrm{eV}\cdot\text{Å}^{-1}.$$

In contrast to (15) the values obtained for the electron-phonon interaction for the β_{2g} and β_{3g} vibrations are not different, since the difference is determined by the small splitting of the $|B_{2u}\rangle$ and $|B_{3u}\rangle$ states by the static crystal field. One could probably obtain agreement between calculation and experiment if, in the description of the dynamic interaction of the $(\text{halogen})_2^-$ molecule with the surroundings, the surroundings were taken into account from a microscopic point of view.

Let us now evaluate the contributions to the spin-lattice relaxation from the hyperfine-interaction mechanisms. We obtain A^c by substituting the values $r_0 = 2.94$ Å, $a^* = 0.627$ Å, and $a_1 = 392$ MHz, obtained from Ref. 13, into formula (12), and we obtain A^d using the electron-phonon interaction constant (15) (see Table I). The constant A^d is anisotropic and, since it is an order of magnitude smaller than A^c, this mechanism is unimportant. The value of A^c is in good agreement with the experimentally determined value of A, which is isotropic and only larger by a factor of two.

Thus, both the experimental calculations and the experimental determination that the spin-lattice relaxation rate is independent of the concentration of centers allows us to state that the relaxation rate that we have measured is characteristic of the V_k center itself.

CONCLUSION

There is as yet no satisfactory theory of V_k centers that takes into account with sufficient accuracy the effect of vibrations on the electric field at the position of the V_k center. By comparing a simple model with experiment we were able, however, to show that at a low concentration of centers the measured single-phonon spin-lattice relaxation takes place as a result of the basic mechanisms that have been established for isolated paramagnetic centers. The V_k center is of interest as a single, simple, molecular center which exists in an ionic crystal and for which it is known at the present time that the modulation of the hyperfine interaction and the Kronig–Van Vleck mechanism give comparable contributions to the spin-lattice relaxation. In the case of oxygen molecules in alkali halide crystals, one can consider only the Kronig–Van Vleck mechanism.[16,20] In the case of the CaO_3 molecule in calcite only the hyperfine interaction is important.[21] Moreover, in the alkali halides the V_k centers represent a variety of cases with widely differing parameter ratios, λ/Δ which must be manifest in a variety of cases of anisotropy of the spin-lattice relaxation rate.

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