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Raman process in the spin-lattice relaxation of F centers in alkali halides. Theory and optical measurements*

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The temperature dependence of the spin-lattice relaxation time of F centers in KBr is investigated between 6 and 15°K. The observed values of T_1^{-1} can be fitted by a law of the form $T_1^{-1} = BT^7 + CT^9$ with B and C independent of field in the range from 400 to 1800 G. A theory is given based on the modulation of the hyperfine interaction, which accounts for the main relaxation mechanism responsible for this T^7 term.

I. INTRODUCTION

The spin-lattice relaxation of F centers in alkali halides has been the subject of numerous papers and proper attention was given to both experiment[1-5] and theoretical[5-10] problems by different authors particularly in the last ten years. As a result, the following conclusions, regarding the very-low-temperature behavior of the relaxation time, appear to be presently well established.

(i) The dominant relaxation mechanism arises from the phonon modulation of hyperfine interaction between the F electron and the nuclei of the neighbor ions on the first two coordination spheres. This gives

$$T_1^{-1} \propto H^3 \coth(g\mu_B H/2kT) .$$

(ii) A competitive mechanism due to the combined effect of ligand-field modulation and spin-orbit interaction becomes dominant at fields higher than approximately 20 kG. Thus leading to an $H^5 \coth(g\mu_B H/2kT)$ dependence of T_1^{-1} at the highest fields.

(iii) The intrinsic relaxation times are observed only in highly diluted samples, and so the highly sensitive optical techniques are indicated for its measurement.

(iv) The best results on the calculations are obtained using the Gourary and Adrian type-III wave function for the F center.[11]

The above conclusions certainly apply to the direct or one-phonon processes, for which theoretical expressions for the spin-lattice relaxation time T_1 were obtained employing parameters coming from independent measurements of other F-center properties. These calculations can account for the observed experimental values of T_1 measured by standard microwaves techniques in KCl by Feldman, Warren, and Castle[1] (FWC), confirmed by Panepucci and Mollenauer[5] (PM) by magneto-optical techniques, who also extended the measurements to KBr and KI and recently verified in caesium and sodium halides.[12] In the case of the two-phonon process the amount of available information is more reduced, particularly as far as the experimental data due to the intrinsic limitations of the microwaves techniques. As a result the only reliable data on the temperature dependence of T_1 are those obtained by FWC which again refer only to KCl.

In view of the above it appeared convenient to extend the analysis of the temperature dependence of T_1 to other alkali halide to further check the assumptions made in the calculations, by seeing whether or not the observed times would properly scale with the corresponding parameters in two different systems, as they do for the direct process PM.[5]

In this paper we present the results of optical measurements of T_1 against temperature for F centers in KBr in the temperature range between 6 and 15 °K together with calculations made for the two-phonon process along the same lines followed in PM[5] for the direct process.

The final expressions are put in terms of known parameters in order to allow comparison between different systems.

II. EXPERIMENTAL

The samples were prepared by cleaving KBr single crystals grown from the melt by the Czochralski method and additively colored in a potassium atmosphere at 600 °C.[13] The F-center concentration was measured from the optical density by means of Smakula's formula.[14] A Cary 17 spectrometer was used for this purpose and the concentration of the samples was found to be 8×10^{15} F centers/cm^3.

No significant amount of other centers were detected. The samples were mounted in a holder attached to a cold finger within a Janis Research Co. helium cryostat. The sample temperature was controlled by a heater placed in the sample holder, and temperature measurements were made using a calibrated Allen Bradley resistor and a Keithley Model 520 low-dissipation resistance bridge.

Following the technique described in Ref. 5, the measurements of T_1 were made by monitoring the recovery of the magnetic-circular-dichroism (MCD) signal after a short pulse of circular polarized light had produced a transient magnetization of the sample.

The optical apparatus employed, similar to that used by PM,[5] is shown in Fig. 1. The light monitor beam was alternating between σ^+ and σ^- polarization states by a commerically available unit (photoelastic modulator Morvue Electronic System PEM-3) following a Jarrel-Ash $\frac{1}{2}$-m monochromator, and the modulated transmitted intensity was detected by an EMI 9558 QB photomultiplier tube fed by a HP 6516 dc high-voltage power supply modified by a feed back loop to give constant anode tube current.

The optical pumping was accomplished using a 500-W high-pressure mercury-arc lamp, followed by a 5800-Å interference filter having a 100-Å bandwidth.

The pumping beam entering the system at right angles was first reflected and then polarized by a mirror and a circular polarizer assembly (actuated by a selenoid). When in pumping position the mirror also acted as a shutter thus preventing the pumping light from saturating the photomultiplier. A narrow-band interference filter centered at 6328 Å monitoring wavelength was also placed in front of the photomultiplier tube to further protect it.

Since the pumping beam was polarized after reflection, no special care was necessary to achieve high polarization efficiency. Furthermore the monitor beam light path was straight thus eliminating any possible spurious polarization effects from reflecting surfaces. Magnetic fields up to 1.8 kG were produced by a small electromagnet with hollow pole caps. When the signal-to-noise ratio had to be improved, such as for the shortest relaxation times, a HP 5480B signal averager synchronized with the pumping light pulse was used.

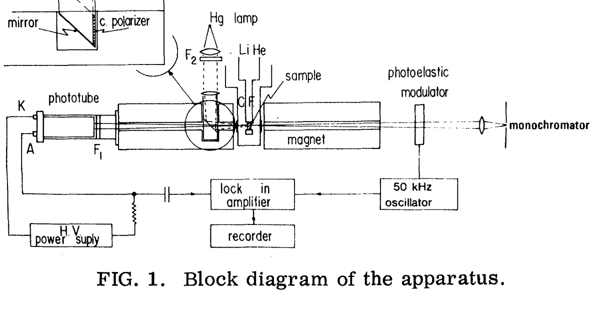

FIG. 1. Block diagram of the apparatus.

III. THEORY

The theory given in PM[5] for the direct process can easily be extended to account for the temperature dependence of the spin-lattice relaxation time of the F centers in alkali halides. As in PM[5] we shall assume that the main coupling between the lattice and the electron spin comes from the phonon modulation of hyperfine interaction. Since the isotropic contact term accounts for 90% of this interaction,[15] we shall disregard the anisotropic part due to the dipole-dipole term and write the H_{hfs} Hamiltonian as

$$H_{\text{hfs}} = \sum_m \alpha_m \vec{I}_m \cdot \vec{S}\, |\psi(r_{lm})|^2 , \tag{1}$$

where

$$\alpha_m = a_m |\psi(r^0_{lm})|^{-2} ,$$

where a_m is the hfs constant for the nucleus of spin I_m at site m. $\psi(r_{lm})$ is the value of the electron wave function at the nucleus position which we assume to be a function only of distance r_{lm} between the nucleus at site m and vacancy at site l. $\psi(r^0_{lm})$ is the value of $\psi(r_{lm})$ at the ions equilibrium position. The lattice vibrations will introduce relative displacements

$$\vec{u}_{lm} = \vec{r}_{lm} - \vec{r}^{\,0}_{lm} . \tag{2}$$

Expanding (1) in series of this relative displacement, Eq. (2), we can write the time-dependent part of (1) as

$$\begin{aligned} H_{\text{int}} &= H_{\text{hfs}}(t) - H_{\text{hfs}}(0) = (\vec{u}_{lm} \cdot \vec{\nabla}) H_{\text{hfs}} + \tfrac{1}{2} (\vec{u}_{lm} \cdot \vec{\nabla})^2 H_{\text{hfs}} \\ &= H^{(1)}_{\text{int}} + H^{(2)}_{\text{int}} + \cdots , \end{aligned} \tag{3}$$

where $H^{(1)}_{\text{int}}$ and $H^{(2)}_{\text{int}}$ refer to the linear and quadratic terms in the displacement $\vec{u}_{lm}$, Eq. (2). This will give rise to the two-phonon relaxation process that became dominant in the temperature range that we are concerned with here.

Assuming that the ions in the neighborhood of the vacancy, and thus the center of the vacancy itself, are displaced as the ions in normal lattice site, we can write, PM[5],

$$\vec{u}_{lm} = \vec{u}_l - \vec{u}_m , \tag{4}$$

where $\vec{u}_l$ and $\vec{u}_m$ can be treated in the usual way introducing the normal vibration modes of the lattice and expressed in terms of phonon creation and annihilation operator.[16]

We get

$$\vec{u}_{lm}=\sum_{\vec{f},j}\vec{e}(\vec{f},j)\big[q(\vec{f},j)\big(e^{i(\vec{r}_l\cdot\vec{f}/a)}-e^{i(\vec{r}_m\cdot\vec{f}/a)}\big)+q^{\dagger}(\vec{f},j)\big(e^{-i(\vec{r}_l\cdot\vec{f}/a)}-e^{-i(\vec{r}_m\cdot\vec{f}/a)}\big)\big]\ , \tag{5}$$

where $q(\vec{f},j)$ is the quantum mechanics operator of annihilation of a phonon with phase vector $\vec{f}$,[16] and polarization index j, $q^{\dagger}(\vec{f},j)$ is its Hermitian conjugate, $\vec{e}(\vec{f},j)$ is the unit vector in the direction of polarization, and a is the interionic distance.

In the following we shall use the Debye approximation and assume a single isotropic value v for the speed of sound, which is related to the phonon frequency ω by

$$|\vec{f}|=a\omega/v\ . \tag{6}$$

At temperatures much lower than the Debye temperature most of the phonon satisfies the inequality

$$(\vec{r}\cdot\vec{f})/a\ll 1\ . \tag{7}$$

We shall then expand the exponential in Eq. (5) to first order, and calculate the relaxation rate within this approximation. The effect of taking into account higher-order terms shall be considered afterwards.

Transitions involving two phonons arise in first order from the quadratic term $H_{\text{int}}^{(2)}$ of Eq. (3) and in second order from the linear part $H_{\text{int}}^{(1)}$. Here we shall calculate the transition probability for the first-order process, which can be shown to be the most important.

Using Eqs. (3) and (5) we can write the nonlinear interaction Hamiltonian as

$$H_{\text{int}}^{(2)}=\frac{1}{2}\sum_m \alpha_m\vec{S}\cdot\vec{I}_m\sum_{fj}\sum_{f'j'}(-1)\big[q(\vec{f},j)q(\vec{f}',j')+q^{\dagger}(\vec{f},j)q^{\dagger}(\vec{f}',j')-q(\vec{f},j)q^{\dagger}(\vec{f}',j')-q^{\dagger}(\vec{f},j)q(\vec{f}',j')\big]\frac{\vec{r}_{lm}\cdot\vec{f}}{a}\ \frac{\vec{r}_{lm}\cdot\vec{f}'}{a}$$
$$\times\sum_{\alpha\beta}\big[\vec{e}(\vec{f},j)\cdot\vec{I}_{\alpha}\big]\big[\vec{e}(\vec{f}',j')\cdot\vec{I}_{\beta}\big]\nabla_{\alpha}\nabla_{\beta}|\psi(r_{lm})|^2\ , \tag{8}$$

where $\vec{I}_{\alpha}$ and $\vec{I}_{\beta}$ are unit vectors in the direction of the coordinate axis.

This perturbation can induce transitions between states $|i\rangle$ and $|f\rangle$ such as

$$|i\rangle=|M_s,M_m,n(\vec{f},j),n(\vec{f}',j')\rangle\ ,\qquad |f\rangle=|M_s-1,M_m+1,n'(\vec{f},j),n'(\vec{f}',j')\rangle \tag{9}$$

where the occupation numbers which remain unchanged have been omitted. In this elementary process, the electron spin of the mth nucleus and the phonon occupation numbers $n(\vec{f},j)$ and $n(\vec{f}',j')$ are changed by one unit.

The transition probability for this process is given in first-order perturbation theory by

$$P_{+-}(M_m,\vec{f},j,\vec{f}',j')=(2\pi/\hbar)\langle i|H_{\text{int}}^{(2)}|f\rangle\times\langle f|H^{(2)}|i\rangle\delta(E_i-E_f)\ . \tag{10}$$

The matrix element of (8) between product wave functions like Eq. (9) will be the product of a spin and a phonon factors. We have for the spin factor

$$|\langle-\tfrac{1}{2},M_m+1|\alpha_m\vec{I}_m\cdot\vec{S}|\tfrac{1}{2},M_m\rangle|^2=\tfrac{1}{4}\alpha_m^2(I_m+M_m+1)(I_m-M_m)\ . \tag{11}$$

As for the phonon factor we first note that two types of phonon operators are present in Eq. (8). Those involving only the two creation or annihilation operators will be associated with the resonant absorption or emission of phonon $\omega_{\vec{f}j}$ and $\omega_{\vec{f}'j'}$ such that

$$\hbar\omega_{\vec{f}j}+\hbar\omega_{\vec{f}'j'}=\Delta E\simeq g\mu_B H\ . \tag{12}$$

Only those phonon modes having $\hbar\omega<g\mu_B H$ will be operative for this resonant process. Since this number is a negligible part of the thermal equilibrium phonon spectrum we can disregard this contribution.

We are thus left in Eq. (8) only with the crossed product $qq^{\dagger}$ for which the matrix element gives

$$|\langle n(\vec{f},j)-1,n(\vec{f}',j')+1|q(\vec{f},j)q^{\dagger}(\vec{f}',j')|n(\vec{f},j),n(\vec{f}',j')\rangle|^2=(\hbar/2M)^2[n(n'+1)/\omega\omega']\ , \tag{13}$$

where M is the mass of the crystal.

Almost any phonon mode can contribute through this term since conservation energy in this case only imposes that the difference in energy between the created and destroyed phonon matches the spin-flip energy that is

$$\hbar\omega'-\hbar\omega=g\mu_B H\ . \tag{14}$$

This gives rise to the Raman relaxation process which is therefore dominant at all but the very low temperatures.

To obtain overall transition rates we must first sum Eq. (10) over all initial and final phonon states, that is, over $\vec{f},j$ and $\vec{f}',j'$. To do this we replace the dot products in Eq. (8) by their average over all propagation and polarization direction and replace the summations $\sum_{\vec{f},j}\sum_{\vec{f}',j'}$ by double integration over the whole Debye frequency domain including the appropriate density of states

$$N(\omega) = (3V/2\pi^2)\omega/v^3 \ , \tag{15}$$

where V is the volume of the crystal.

After the first integration over ω' and noting that

$$\omega' = \omega + g\mu_B H/\hbar \simeq \omega, \tag{16}$$

because $g\mu_B H \ll \hbar\omega$ for most phonons, we obtain

$$P_{+-}(M_m) = \frac{\pi\alpha_m^2(I_m + M_m + 1)}{81\hbar^2 v^4}(I_m - M_m)\int_0^{\omega_D} N(\omega)n(n+1)\,\omega^4 r_{lm}^4\left|\sum_{\alpha\beta}\nabla_\alpha\nabla_\beta|\psi(r_{lm})|^2\right|^2 d\omega \ . \tag{17}$$

The above expression gives the transition probability between states $|M_s, M_m\rangle$ and $|M_s - 1, M_m + 1\rangle$. The actual thermal equilibrium relaxation rate due to the simultaneous flip of the electron and the mth nucleus is obtained from Eq. (17) by taking its thermal average which is simply done by replacing the occupation numbers $n(\omega)$ by its equilibrium values

$$\bar{n}(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1} \ , \tag{18}$$

and summing over all possible initial states M_m weighted by their probability which can safely be taken to be equal to $1/(2I_m + 1)$ for all M_m. The resulting expression can be summed over all nucleus to give the overall relaxation rate. Since we are considering all nuclei in a given shell to be magneticaly equivalent, one has for the N_s nuclei in the sth shell

$$\begin{aligned} W_{+-}(s) &= h^2\sum_s N_s I_s(I_s+1)\nu_s^2/2^2 3^3(2\pi)^3\rho^2 v^{10} \\ &\times\int_0^{\omega_D}\omega^6 n(n'+1)\,d\omega \\ &\times\frac{r_s^4}{|\psi(r_s^0)|^4}\left|\sum_{\alpha\beta}\nabla_\alpha\nabla_\beta|\psi(r_s)|^2\right|^2 \ , \end{aligned} \tag{19}$$

where we have written ν_s for the value of α_s expressed in hertz.[15] We must now calculate the derivatives of the F electron wave function $|\psi(r_{lm})|^2$ appearing in Eq. (19). Following PM[5] we use type-III Gourary-Adrian wave function[11] Φ_F orthogonalized to all the i orbitals of each of the m ions ϕ_{im},

$$\psi(\vec{r}_{lm}) = \frac{1}{N}\left(\Phi_F(r_s) - \sum_{im}\langle\Phi_F|\phi_{im}\rangle\phi_{im}\right) \ . \tag{20}$$

From this, it can be shown[17] that the electron density at nucleus m is given by

$$|\psi(r_m)|^2 = A_m|\Phi_F(r_m)|^2 \ , \tag{21}$$

where A_m, called the amplification factor, depends only on the electronic structure of the mth ion, and Φ_F is[11]

$$\Phi_F = K_m(a/\eta r_{lm})e^{-\eta r_{lm}/a} \ , \tag{22}$$

where η is a parameter that is obtained minimizing the energy.[11] Thus, $|\psi|^2$ is a function of $|\vec{r}_{lm}|^2$ only, and the partial derivatives can be put as

$$\begin{aligned} &\sum_{\alpha\beta}\left(\frac{\partial}{\partial x_\alpha}\frac{\partial}{\partial x_\beta}|\psi(r_{lm})|^2\right)^2 \\ &\quad= \left(\frac{\partial^2}{\partial r^2}|\psi(r_{lm})|^2\right)^2 + \frac{2}{r_{lm}^2}\left(\frac{\partial}{\partial r}|\psi(r_{lm})|^2\right)^2 \\ &\quad= 4\left(\frac{2\eta^2}{a^2} + \frac{4\eta}{ar_{lm}} + \frac{3}{r_{lm}^2}\right)^2|\psi(r_{lm}^0)|^4 \\ &\qquad+ \frac{2}{r_{lm}^2}\left(\frac{1}{r_{lm}} + \frac{\eta}{a}\right)^2|\psi(r_{lm}^0)|^4 \ . \end{aligned} \tag{23}$$

The integral in Eq. (19) gives

$$\int_0^{\omega_D}\frac{\omega^6\exp(\hbar\omega/kT)}{[\exp(\hbar\omega/kT) - 1]^2}\,d\omega = \left(\frac{kT}{\hbar}\right)^7 J_6(T, \Theta_D) \ , \tag{24}$$

where

$$J_6(T, \Theta_D) = \int_0^{x_D}\frac{x^6 e^x}{(e^x - 1)^2}\,dx \ ,$$

which, for temperatures much lower than the Debye temperature Θ_D can be approximated by 6! For example, the error of this approximation is 10% in KCl even at 20 °K.

Within the approximation equation (16) used in evaluating Eq. (17) we have

$$W_{+-} \simeq W_{-+} \ . \tag{25}$$

Thus the final expression for T_1^{-1} becomes

$$T_1^{-1} = 2W_{+-} = \frac{h^2}{108\pi^3\rho^2 v^{10}}\sum_s N_s\nu_s^2 I_s(I_s+1)r_s^4\left[\left(\frac{2\eta^2}{a^2} + \frac{4\eta}{ar_s} + \frac{3}{r_s^2}\right)^2 + \frac{1}{2r_s^2}\left(\frac{1}{r_s} + \frac{\eta}{a}\right)^2\right]\left(\frac{kT}{\hbar}\right)^7 J_6(T, \Theta_D) \ . \tag{26}$$

By taking the expansion of the exponentials in Eq. (3) to third order, new terms appear in Eq. (26), having T^9 and T^{11} temperature dependences. A negative coefficient is predicted for T^9, at least 177 times smaller than the coefficient of T^7; and a positive coefficient for T^{11}, at least 10^5 times smaller.

The appearance of negative terms in the temperature expansion of T_1^{-1}, which has also been predicted by Zevin,[8] should not be surprising, since they are only a part of the power expansion of a positive function of temperature and do not correspond to an independent relaxation process.

Besides the failure of the long-wave approximation, a T^9 term could be due to the so-called phonon-assisted Van Vleck mechanism, as for most Kramers systems.

IV. RESULTS

Figure 2 shows the results of our measurements of T_1^{-1} versus temperature in the range from 6 to 15 °K at a magnetic field of 1300 G. Since one of the problems found in earlier work in spin-lattice relaxation with F centers has been to assure intrinsic relaxation behavior, we checked our samples by performing measurements of the field dependence of T_1^{-1} at low temperatures and fields below 1 kG. This showed that our samples presented no extrinsic behavior, such as that due to aggregates at the fields of interest in this work. Furthermore, the decay curves proved to be true exponentials with a single decay time in all cases.

According to the discussion of Secs. I–III, one could expect the temperature dependence of T_1^{-1} to be of the form

$$T_1^{-1} = BT^7 + CT^9 , \qquad (27)$$

within the investigated range of temperatures. This function is plotted in Fig. 2, using values of B and C adjusted by a least-squares method to give the best fitting to the experimental data. The values of these parameters are given in Table I together with the computed value of B from Eq. (26). Table I also gives the value of the coefficient of T^7 from Ref. 1 for KCl, and its theoretical estimate from Eq. (26). In evaluating Eq. (26) the values of the quantities appearing there were taken from Table II in Ref. 5.

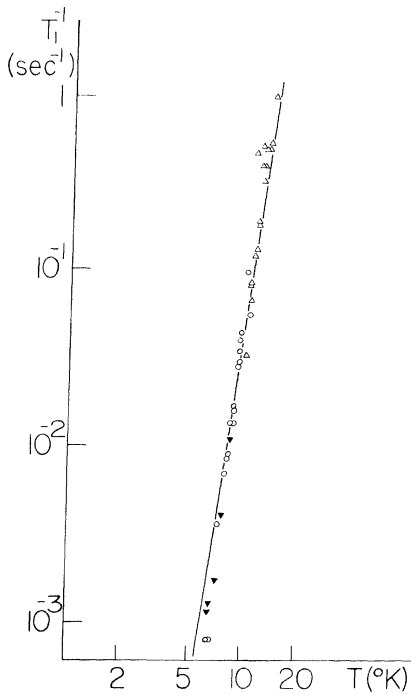

FIG. 2. Experimental values of the relaxation rates of F centers in KBr vs temperature at 1300 G. The solid line represents Eq. (27) with the best-fitting parameters.

If instead of Eq. (27) one uses a single power law to fit the data in Fig. 2, one finds

$$T_1^{-1} = 2.2\times10^{-10} T^{8.22} , \qquad (28)$$

which, within the investigated temperature range, coincides with Eq. (27) which explains the straight appearance of the line drawn in Fig. 2.

V. DISCUSSION

As pointed out in Sec. I, one of the aims of this work was to find whether the modulation of the hfs, which was shown to be the dominant mechanisms at low temperatures, was still responsible for the observed relaxation rates at higher temperatures. From the theoretical and experimental results summarized in Table I we can say that, up to the highest temperatures investigated here, the hfs mechanism can account for the observed rates. In fact the calculated values of B are in fairly good agreement with those observed experimentally.

Furthermore, we have found that for fields less than 1.8 kG the observed times are independent of the magnetic field strength, as expected for this mechanism. On the other hand, it must be observed that, even with the very low scatter of points obtained with the optical technique, the data in Fig. 2 do not allow a definite conclusion about the presence of a T^9 process. In fact, reasonable fitting could still be obtained using either single-power functions such as BT^7 or CT^9, although the goodness of the fittings as measured by the square of the deviations was poorer in the last case. Thus the choice of the form of Eq. (27) must be thought as a plausible one, based upon theoretical considerations, rather than a conclusive result from the experiment.

TABLE I. Experimental values B_{expt} and C_{expt} obtained from best fitting of Eq. (27) and comparison with B_{theor} calculated from expression (26).

	B_{expt} ($^\circ$K^{-7} sec^{-1})	B_{theor} ($^\circ$K^{-7} sec^{-1})	C_{expt} ($^\circ$K^{-9} sec^{-1})
KBr	4×10^{-9}	1.5×10^{-8}	10^{-11}
KCl	2.9×10^{-9} [a]	5.3×10^{-10}	

[a] Reference 1.

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