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Spin-lattice relaxation of *F* centers in Na and Cs halides

R. A. Carvalho,* M. C. Terrile, and H. Panepucci

Departamento de Física e Ciência dos Materiais, Instituto de Física e Química de São Carlos, Universidade de São Paulo, 13560 São Carlos, SP, Brazil

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We report the measurements of spin-lattice relaxation times T_1 of *F* centers in NaCl, NaBr, CsBr, and CsCl. The experiments were carried out at liquid-helium temperatures and magnetic fields up to 15000 G. The results are shown to be in agreement with the relaxation rates predicted by the model proposed by Panepucci and Mollenauer.

INTRODUCTION

The magneto-optical methods have proved to be the most appropriate for measuring electronic spin-lattice relaxation times T_1 of *F* centers.[1]

At very low temperatures the magnetic circular dichroism (MCD) of *F* centers is proportional to its ground-state polarization.[1,2] When this polarization is removed from its thermal-equilibrium value, the MCD signal can be used to follow the recovery of the magnetization of the sample until thermal equilibrium is reached. Thus, T_1 can be easily measured. Using this very sensitive optical method we measured T_1 for *F* centers in Na and Cs halides for different magnetic fields.

In Ref. 1 similar measurements were performed in potassium halides, and a theoretical expression was derived which accounts for experimental values of T_1 in the potassium halides, explaining its dependence on the properties of the halide ions. Since the results in Ref. 1 also predict the dependence of T_1 on the alkali ions and the crystal structure, it was desirable to further test its validity by measuring the field dependence of T_1^{-1} in other than potassium salts, including those cesium halides which have a different structure.

EXPERIMENTAL

The NaCl and NaBr crystals were grown by Czochralski method. The first one was additively colored in a K atmosphere at[3] 600 °C from which a sample having ~3.5×10^{16} *F* centers/cm^3 was cleaved. Harshaw CsCl and CsBr crystal samples were cut and polished in a dry N_2 atmosphere; these and the NaBr sample were colored by tungsten x-ray irradiation, that produced ~10^{16} *F* centers/cm^3. In all cases care was taken to avoid the exposure of the samples to light and moisture before cooling. The *F*-center concentrations were determined by Smakula's formula[4] using a Cary 17 spectrophotometer. The optical spectra showed no significant amount of other centers.

The samples were mounted inside a small superconducting NbZr solenoid adapted to a Janis Research Co. Model DT immertion-helium cryostat. Most measurements were performed at 1.8 °K that was the lowest temperature attainable with out equipment. The measurements of T_1 were done by recording the MCD signal after a transient magnetization of the sample. The last could be done either by (a) a high-intensity pulse of circulary polarized light along the applied *H* field; (b) thermalizing the sample at a very high (or very low) magnetic field, and then changing it to a desired final value. In most of our measurements the last method was prefered since the small NbZr solenoid could be energized up to its maximum field of 17 kG in a time shorter than T_1. An exponential recovery of the MCD signal was found in all cases.

In order to find the best wavelength for either the monitor beam or the pumping beam, the MCD signal was recorded versus wavelength as shown in Fig. 1 for CsCl.

The experimental setup is shown in Fig. 2. The polarization state of a collimated monitor beam,

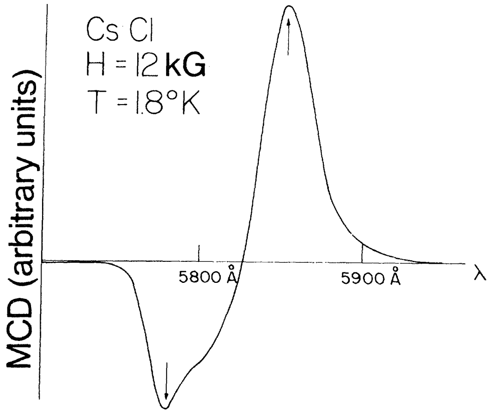

FIG. 1. Magnetic-circular-dichroism signal for the *F* center in CsCl. The arrows show the best wavelengths for detection of the MCD signal.

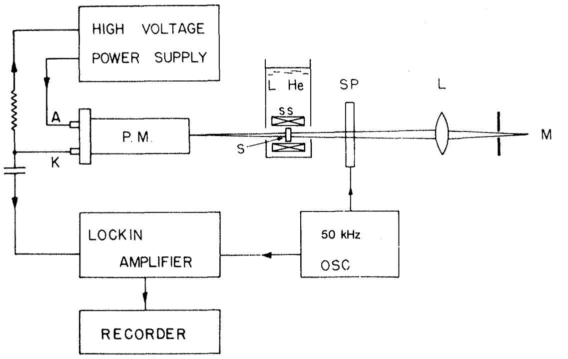

FIG. 2. Block diagram of the apparatus. SP, stress plate modulator; S, sample; SS, superconductivity solenoid.

coming from a Jarrel-Ash $\frac{1}{2}$-m monochromator, was chopped between right circular σ^+ and left circular σ^- by a commercial photoelastic modulator unit (Morvue Electronic Systems). The intensity of the transmitted light was detected by an EMI 9558QB photomultiplier tube fed by a HP 6516 dc high-voltage power supply modified by a feed back loop to give constant average anode current operation. The response of this feedback was made sufficiently slow to allow response at the 50-kHz modulation frequency.

RESULTS AND DISCUSSION

The theoretical expression derived in Ref. 1 for T_1^{-1} was based on the modulation of hyperfine interaction by the lattice vibrations. In the pumped liquid-helium range ($T < 4$ °K), where the direct process is dominant, the predicted relaxation rate is[1]

$$T_1^{-1} = \frac{16\pi^3}{9}\frac{1}{\rho v^5}\frac{g^3\mu_B^3 H^3}{h^2} \times \sum_s N_s \nu_s^2 I_s(I_s+1) r_{ls}^2 \left(\frac{1}{r_{ls}} + \frac{\eta}{a}\right)^2 \coth\frac{g\mu_B H}{2kT} = AH^3 \coth\frac{g\mu_B H}{2kT}\,, \qquad (1)$$

where s indicates the coordination sphere with N_s ions, each at a distance r_{ls} from the center of the vacancy and having nuclear spin I_s. μ_B is the Bohr magneton, h is the Planck's constant, and a is the interionic distance.

The parameters in (1) were taken from independent experimental results and are given in Table I. For the speed of sound we use the transversal velocity calculated with $v = (C_{44}/\rho)^{1/2}$. The elastic stiffness constant C_{44} and the density ρ of the crystal were obtained from references indicated in Table I. η is a parameter that enters in type-III Gourary-Adrian[7] wave function for the F-center ground state. In our calculations we used η values interpolated from data included in the same reference. It is worth emphasizing that η has almost the same value for different alkali halides. The g factor is measured in electronic-paramagnetic-resonance experiments; ν_s is the hyperfine interaction constant between the F-electron and the s-shell nuclei in Hz, and is obtainable in electron-nuclear-double-resonance (ENDOR) experiments.

We could not find ENDOR data for NaBr, CsCl, and CsBr salts. For NaBr we estimated the ν_s values from those corresponding to NaCl, KCl, and KBr. In fact, the isotropic hyperfine interaction is given by

$$h\nu_m = \tfrac{8}{3}\pi g \mu_B g_m^N \mu_m^N |\psi(r_{lm})|^2, \qquad (2)$$

where g_m^N and μ_m^N are the gyromagnetic factor and

TABLE I. Parameters employed in the theoretical calculations.

Structure		ρ (g/cm^3)	C_{44} (10^{11} dyn/cm^2)	ν_1 (MHz)	ν_2 (MHz)	η	g_{zz}	N_1	N_2	I_1	I_2
NaCl	NaCl	2.210 [a]	1.331 [a]	61.5 [b]	12.5 [b]	2.38 [c]	1.987 [d]	6	12	$\frac{3}{2}$	$\frac{3}{2}$
NaBr	NaCl	3.299 [a]	1.070 [a]	55	65	2.41	1.994 [e]	6	12	$\frac{3}{2}$	$\frac{3}{2}$
CsCl	CsCl	3.9880 [f]	0.804 [f]			2.73		8	6	$\frac{7}{2}$	$\frac{3}{2}$
CsBr	CsCl	4.6550 [g]	0.999 [g]	138.6 [h]		2.81	1.9840 [h]	8	6	$\frac{7}{2}$	$\frac{3}{2}$

[a] Reference 5.
[b] Reference 6.
[c] Reference 7.
[d] Reference 8.
[e] Reference 9.
[f] Reference 10.
[g] Reference 11.
[h] Reference 12.

the nuclear magneton of the mth ion, respectively.

For $\psi(r_{lm})$ we used the type-III Gourary-Adrian[7] wave function $\phi_F(r_{lm})$ orthogonalized to all orbitals of the neighbor ions. It can be shown that $|\psi(r_{lm})|^2 = A_m |\phi_F(r_{lm})|^2$,[6,13] where A_m is an amplification factor which depends on the electronic structure of the mth ion only, and

$$\phi_F(r_{lm}) = K(\eta)(a/\eta r_{lm})e^{-\eta r_{lm}/a}, \tag{3}$$

where $K(\eta)$ is a constant.[7]

As we pointed out before, the η's are very similar for those salts and the same can be said for the interionic distance a. Thus $|\phi_F(r_{lm})|^2$ is roughly the same in all alkali halides considered here.

With these approximations, using (2) and disregarding small differences in g, we can write

$$\frac{\nu_{\mathrm{Na}}(\text{in NaBr})}{\nu_{\mathrm{K}}(\text{in KBr})} \simeq \frac{g^N_{\mathrm{Na}}\mu^N_{\mathrm{Na}}A_{\mathrm{Na}}}{g^N_{\mathrm{K}}\mu^N_{\mathrm{K}}A_{\mathrm{K}}}, \tag{4}$$

and similarly

$$\frac{\nu_{\mathrm{Br}}(\text{in NaBr})}{\nu_{\mathrm{Cl}}(\text{in NaCl})} \simeq \frac{g^N_{\mathrm{Br}}\mu^N_{\mathrm{Br}}A_{\mathrm{Br}}}{g^N_{\mathrm{Cl}}\mu^N_{\mathrm{Cl}}A_{\mathrm{Cl}}}. \tag{5}$$

The values of the amplification factors are known from ENDOR experiments[6] in KCl, KBr, and NaCl from which the frequencies given in Table I are calculated using (4) and (5).

The ν_s for the Cs ions in CsCl was obtained from the resolved hyperfine structure of the EPR spectrum,[12] and the same value was assumed for CsBr according to the above arguments.

Furthermore, since the first eight-neighbor Cs nuclei have the highest magnetic moment, we can disregard the contributions due to the next-nearest neighbors.

Figure 3 shows the experimental results for Cs and Na halides at 1.8 °K as a function of the magnetic fields. Here the solid lines represent the empirical equation

$$T_1^{-1} = (AH^3 + BH^5)\coth(g\mu_B H/2kT) \tag{6}$$

where A and B are the best-fitting parameters adjusted using a multiple regression method. In fitting the data, we disregarded those low-field points which show an extrinsic relaxation behavior.[14]

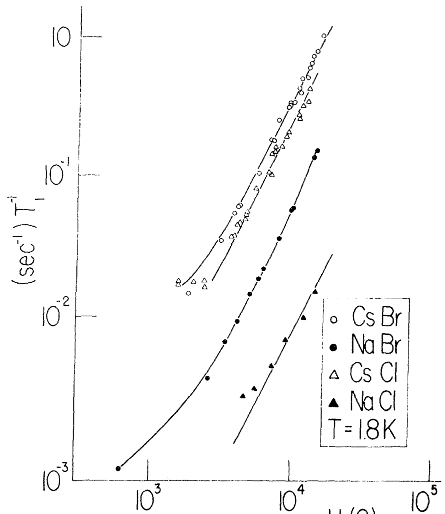

FIG. 3. Experimental relaxation rates for the F center in NaCl, NaBr, CsCl, and CsBr. The solid lines represents the best fitting curves. Note the small influence of the halide ions in the Cs salts as compared with the Na salts.

The experimental values of A thus obtained are given in the third column in Table II where we included also data for potassium halides from Ref. 1. The effect of the cation increasing magnetic moment in going from K to Cs is evident from this result.

As expected this effect is more accentuated in the case of the chlorides since the second shell does not contribute significantly to the relaxation rates in this group of salts. On the other hand, the bromine nuclei in the second shell are seen to dominate the relaxation rates in KBr and NaBr, again as expected.

Both cesium salts give very close relaxation rates, which shows the consistency of our as-

TABLE II. Experimental and theoretical values of the parameters in Eq. (6).

	T (°K)	A_{expt} ($\mathrm{G}^{-3}\ \mathrm{sec}^{-1}$)	A_{theor} ($\mathrm{G}^{-3}\ \mathrm{sec}^{-1}$)	B_{expt} ($\mathrm{G}^{-5}\ \mathrm{sec}^{-1}$)	B_{theor} ($\mathrm{G}^{-5}\ \mathrm{sec}^{-1}$)
KCl	1.6 [a]	3.5×10^{-16}	7.9×10^{-17}	7.2×10^{-24}	1.4×10^{-25}
NaCl	1.8	2.8×10^{-15}	2.9×10^{-15}	3.0×10^{-24}	1.9×10^{-25}
CsCl	1.8	3.1×10^{-13}	7.4×10^{-13}	1.0×10^{-22}	2.2×10^{-24}
KBr	1.6 [b]	1.1×10^{-14}	2.4×10^{-15}	1.7×10^{-23}	3.0×10^{-24}
NaBr	1.8	1.7×10^{-14}	5.8×10^{-14}	2.5×10^{-23}	1.5×10^{-25}
CsBr	1.8	3.4×10^{-13}	7.4×10^{-13}	4.1×10^{-21}	2.1×10^{-24}

[a] Reference 15.

[b] Reference 1.

sumption in taking the Cs hyperfine interaction equal in both salts. The slightly faster rate in CsBr is due to the second shell contribution.

Comparison with the theoretical values of A calculated from Eq. (1), which are given in the fourth column in Table II, shows that this expression can reasonably predict the relaxation rates for F centers, accounting for the effect of both, cation and anion in either the NaCl or the CsCl structure.

The last two columns in Table II give the experimental and calculated values of B. Unfortunately, due to the limitation in the highest available field in our experiments, the determination of this coefficient is much less accurate than in the case of A and should be taken as an order of magnitude estimate. The theoretical values were derived from a theory based on the phonon modulation of the g values. This theory, to be reported in detail elsewhere, leads to the following approximate expression for B:

$$B = 3.32\times 10^{-3}(g^3\mu_B^5/\hbar^4)(\Delta g)^2/\rho v^5), \tag{7}$$

where $\Delta g = g - g_e$ are corresponding g shifts for the F centers. The results approximately agree with the experiment, allowing one to conclude that this relaxation mechanism must be weak enough, so that its effects should only become important at fields in excess of 10 kG.

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*Universidade Federal de São Carlos 13560 São Carlos SP, Brazil.

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