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Spin-lattice relaxation of F centers in mixed alkali halides: KBr_xCl_{1-x}

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Measurements of the spin-lattice relaxation time, T_1, of F centers in mixed alkali halide crystals, KBr_xCl_{1-x}, have been made using magneto-optical techniques: magnetic circular dichroism (MCD) and optical pumping. These techniques consist of monitoring the recovery of the MCD signal to equilibrium, after an intense pulse of circularly polarized light. They were used to obtain the dependence of T_1 on the magnetic field up to 6.5 T and for several relative halide concentrations x at pumped liquid-He temperature (2 K). A computer-assisted system designed to measure relaxation pulses of the order of 1 ms is described. A model based on phonon modulation of the hyperfine interaction was modified to introduce the relative concentration x. This proves to be the main mechanism for spin-lattice relaxation for the temperature and magnetic-field range considered here, as described for unmixed alkali halides.

INTRODUCTION

F centers in alkali halides have been the subject of many investigations.[1–3] They are attractive systems academically since their simplicity allows a better understanding of their behavior and are of technological interest as materials for magnetically tuned masers, optically pumped microwave amplifiers, polarized nuclear targets for neutron scattering, and magnetooptical memories.

An understanding of the spin-lattice relaxation mechanism is fundamental for finding a way to control it. Many papers have been published regarding optical and resonant measurements of the relaxation time and have provided their theoretical explanation.[4] They have considered F centers in many alkali halides with NaCl (fcc) structure and CsCl (bcc) structure, but to our knowledge always in an unmixed matrix. It seems clear[5,6] that phonon modulation of the hyperfine interaction with neighboring nuclei is the main relaxation mechanism, for both direct and Raman phonon processes, at least for moderate magnetic fields ($0.5 < H < 2.5$ T). The modulation of the crystal field by lattice vibrations becomes noticeable above 2.5 T and becomes dominant at higher fields. Naturally, this is true for diluted F centers ($\approx 10^{15}$ centers/cm^3) and reasonably high magnetic field where intrinsic relaxation mechanism dominates.

At low temperatures (liquid helium) only one phonon direct process is important and the temperature and field dependence for the relaxation rate can be adjusted by an expression of the form

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

The first term is expected from the phonon modulation of the hyperfine structure and the second for crystal-field modulation.[7]

With the semiphenomenological theory described in Ref. 7 the coefficient A can be calculated using parameters determined from independent experiments. These values successfully scale the field dependence of T_1 for pure alkali halides. Here, this theory is adapted to take into account mixed crystals, introducing the relative concentration x in the calculation. Compared with the experimental results for $KBr_{1-x}Cl_x$ the field dependence of T_1 fits the experimental data for several orders of magnitude of A and scales properly from $x=0$ to 1. As for the constant B, a model relates its value to the g factor displacement measured in ESR experiments.[8]

The measurements of T_1 as a function of magnetic field must be nonresonant which justifies the use here of magneto-optical methods. As a high sensitivity method, it is also indicated in order to observe the intrinsic behavior of F centers, which requires low concentration. The magnetic circular dichroism (MCD) signal is proportional to the spin polarization of the lowest quantum state, while a pulse of intense circularly polarized light of appropriate wavelength, propagating parallel or antiparallel to the magnetic field, can be used to change this polarization at will.[7] The value of T_1 is obtained from the recovery of the MCD signal to equilibrium after the intense light pulse.

The computer-assisted system designed for signal analysis is also described. It allows the measurement of relaxation times of several minutes, at low magnetic fields and temperatures, and of milliseconds, at high fields.

EXPERIMENTS

Mixed crystals were grown by the Czochralski method for pure KCl and KBr salts, in ten different relative concentrations. A difference of 2% was observed between the concentration in solid solution as measured by ion-sensitive electrodes and that in the melt. The series KCl-KBr was chosen because single crystals can be grown for any concentration.

Samples with $10\times10\times2$ mm^3 were cleaved, colored by x-ray irradiation with a tungsten tube and stored in the dark or at liquid-N_2 temperature. Care was taken to keep the concentration of F centers below 10^{15} centers/cm^3

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and their distribution as homogeneous as possible by filtering the low-energy x ray with 2 mm Al filter and irradiating alternately the two opposite faces of the sample. The optical density was measured using a Cary-17 spectrophotometer. The Smakula formula together with the optical density was used to obtain the *F* center concentration.

The paramagnetic contribution to the magnetic circular dichroism S can be shown to be proportional to the ground-state spin polarization P_e at low temperatures, $S = KP_e$. This means that the spin dynamics can be followed via the evolution of the MCD signal $S(t)$. A high intensity circularly polarized light pulse can remove the spin polarization from its thermal equilibrium value. The spin lattice relaxation time T_1 is then obtained from the exponential evolution of $S(t)$ to equilibrium, after the pumping pulse. The basic system and a description of MCD measurements and optical pumping can be found in Ref. 7.

In the high-magnetic-field region the relaxation times become short, of the order of milliseconds, thus making necessary the introduction of some automation in the excitation, detection, and data acquisition procedure. A scheme of the system is shown in Fig. 1. The ten samples, with distinct values of x, were mounted on a support positioned at the center of a superconducting split coil (Intermagnetics), provided with transverse and axial optical access. Each sample could be positioned to intercept the light path by means of an external handle.

All measurements were performed between 1.92 and 2.10 K. The temperature was controlled and measured via the liquid-He vapor pressure with a Bourdon manometer. The best wavelength for the monitoring and pumping beams was determined, in each case, from the MCD spectra as shown in the upper left corner of Fig. 1.

The measuring beam, with wavelength λ_m, was generated by a tungsten filament source, and a 0.5 m Jarrel-Ash monochromator. Its circular polarization was modulated from right to left by a 50 KHz photoelastic modulator (Morvue Electronic Systems). A photomultiplier tube EMI 9558QB was used for detection. While measuring the MCD spectra, a feedback loop in the high-voltage supply was connected to eliminate low-frequency anode current fluctuations.

The pumping light sources (λ_p) were an Ar ion laser and a dye laser (both Spectra Physics), with the appropriate circular polarization. Two opposite phase electromechanic shutters, S_1 and S_2, controlled the pumping-measuring cycles, preventing phototube saturation and blinding by reflections of the pumping beam.

A triggering pulse from the double timer starts the pumping-measuring cycle. After a delay time Δt, shutter S_2 is opened for the pumping beam while shutter S_1 is closed. A second delay time follows after closing shutter S_2 and then S_1 is opened initiating the relaxation measurement. The signal, after lock-in detection, enters a multichannel analyzer PARC 4203. The decay signal, after being averaged for several cycles, is transferred to a VAX 11/780 minicomputer by a serial RS232 interface between averager and computer. The computer analysis gives the T_1 values from the MCD signal decays and fits the relaxation rate vs H to Eq. (1).

In all cases the decay is pure exponential. Attempts to burn a hole in the MCD spectra were unsuccessful, leading to the conclusion that in this experiment the absorption line is homogeneously broadened and no special configuration was preferred regarding the *F* center neighborhood. Moreover the MCD spectra obtained immediately after pumping were identical, except for a scaling factor, to that obtained before. Obviously the scanning rate used for $S(t)$ was much lower than T_1.

RESULTS AND DISCUSSION

Due to the nature of *F* centers, an electron trapped in a halogen vacancy with an extended wave function, an im-

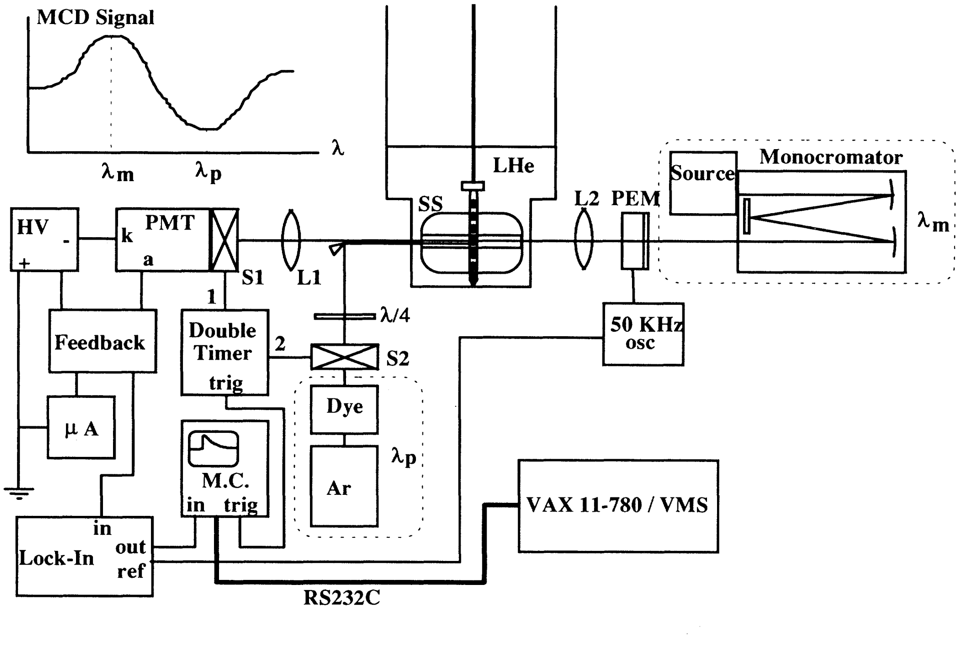

FIG. 1. Block diagram of the MCD spectrometer used for T_1 measurements (see text).

portant interaction between the F electron and the neighboring nuclei occurs, as can be seen in electronic nuclear double resonance (ENDOR) experiments.[9] In fact, interaction even with the 9th neighbors has been detected. On the other hand, the crystal field has little effect on the s-orbital ground state and dipolar interactions are negligible if the centers are diluted (less than 10^{15} centers/cm^3). Thus, the modulation of the hyperfine interaction by lattice vibrations should be the most efficient mechanism for relaxation.

A model for T_1 based on this mechanism is described in detail in Ref. 7. An expression is derived for A in Eq. (1) involving parameters measurable from independent experiments,

$$A=\frac{16\pi^3}{9}\frac{1}{\rho v^5}\frac{g^3\mu_B^3}{\hbar^2}\sum_s N_s\nu_s^2 I_s(I_s+1)r_{ls}^2\left[\frac{1}{r_{ls}}+\frac{2\eta}{a}\right]^2 , \tag{2}$$

where s indicates the first, second, etc., coordination sphere of N_s identical neighbors with nuclear spin I_s at a distance r_{ls} from the center of the vacancy. The lattice parameter a is an experimental parameter.[10] This expression involves the hyperfine structure (hfs) constant ν_s measured in ENDOR experiments, the velocity of sound v calculated from the stiffness constants from c_{44} obtained from ultrasound, the gyromagnetic factor g extracted from ESR results, and the crystal density ρ. The variational parameter η characterizes the Gourary and Adrian type-III function orthogonalized by the Löwdin[11] method to all occupied atomic orbitals, at the neighboring ions.

Following the same steps as in Ref. 7 and introducing the relative concentration as a parameter, the model was adapted for mixed crystals. First, the fact that different classes of centers can exist in mixed crystals must be taken into account. In the case considered here 13 different centers can be formed with identical nearest neighbors K, but having in the second coordination sphere n Cl and $(12-n)$ Br ions, with n varying from 0 to 12.

The probability of occurrence of a center with a specific value of n is given by the binomial distribution

$$W(n)=\frac{12!}{n!(12-n)!}x^n(1-x)^{12-n} , \tag{3}$$

and this is the statistical weight, for a given value of x, the contribution of that class of center to the relaxation. The hfs constant is different for Cl or Br ions indicated as $\nu_{\rm Cl}$ and $\nu_{\rm Br}$, respectively. The nuclear spin is $\frac{3}{2}$, the same for both ions. A linear dependence was assumed for the elastic constant c_{44}. This is justified after a close examination of the phonon dispersion relation for mixed crystals.[12]

The dependence of g, η, and ν_K with x is unknown, but given that these values are quite similar at the extremes $(x=0,1)$, a constant mean value can be used.[9] Naturally the lattice constant a changes with x and so does r_{1s}, with the same dependence, so $\eta(r_{1s}/a)$ can be taken as independent of x, taking the values $\frac{1}{2}\eta$ and $\frac{1}{2}\eta\sqrt{2}$ for the first and second coordination shell, respectively. A linear dependence of the density ρ with x was assumed. Although this is not strictly true,[13] it is a good approximation.

The contribution to T_1^{-1} due to the first neighbor[14] A_1 does not depend on x and is obtained directly from Eq. (2). The contribution of the second shell with 13 classes of centers with n Cl and $(12-n)$ Br can be written as

$$A_2(x)=\frac{16\pi^3}{9h^2}\frac{g^3\mu_B^3(1+\eta\sqrt{2})^2}{\rho(x)v^5(x)}\times\sum_n W(n)[n\nu_{\rm Cl}^2 I_{\rm Cl}(I_{\rm Cl}+1)+(12-n)\nu_{\rm Br}^2 I_{\rm Br}(I_{\rm Br}+1)] , \tag{4}$$

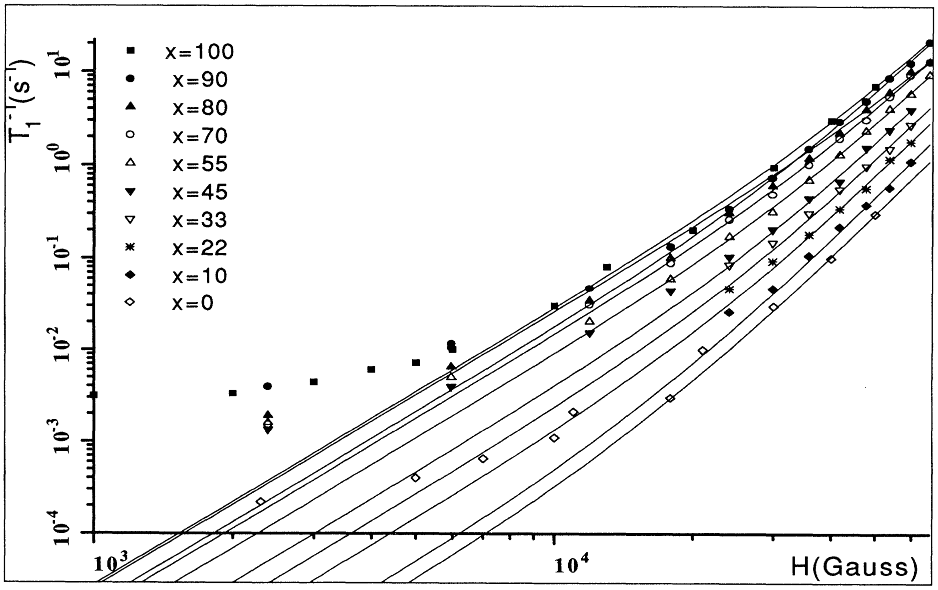

FIG. 2. T_1 dependence on B for ten different concentrations x of $\mathrm{KBr}_x\mathrm{Cl}_{1-x}$. Solid lines represent the best fitted curves of the model given by Eq. (1). The deviation from the model in the low-field region is dependent on the concentration and history of centers, the so-called *extrinsic behavior* described in Ref. 7.

TABLE I. Best fitting parameters.

% of Br	A_E ($s^{-1}G^{-3}x10^{-16}$)	A_T ($s^{-1}G^{-3}x10^{-16}$)	B_E ($s^{-1}G^{-5}x10^{-25}$)
0	4.52	1.93	8.10
10	9.39	4.30	9.90
22	12.3	7.81	17.0
33	20.8	8.90	25.0
45	26.4	10.1	39.0
55	34.9	12.3	68.0
70	54.6	17.0	96.0
80	67.6	19.9	100
90	83.3	21.1	147
100	111	26.4	230

which gives, using the mean of the binomial distribution,

$$\sum_{n=1}^{12} nW(n)=12x \ , \tag{5}$$

and the fact that I_{Br} and I_{Cl} are the same and equal to $\frac{3}{2}$, gives

$$A_2(x)=\frac{80\pi^3}{\hbar^2}\frac{g^3\mu_B^3(1+\eta\sqrt{2})^2}{\rho(x)v^5(x)}(x|\nu_{\mathrm{Cl}}^2-\nu_{\mathrm{Br}}^2|+\nu_{\mathrm{Br}}^2) \ . \tag{6}$$

Disregarding the effect of the outer shells, the constant A was taken as

$$A=A_1+A_2(x) \ . \tag{7}$$

The experimental results for T_1^{-1} as a function of magnetic field up to 6.5 T, for ten different values of x are shown in Fig. 2. Measurements were performed generally at 2 K. At any time that a deviation from this temperature was observed, the corresponding value of T_1 was corrected using Eq. (1), which applies at this low temperature, where direct processes dominate. In all cases a low *F* center concentration (10^{14} centers/cm^3) guaranteed no relaxation through dipole-dipole or superexchange interactions.

The solid lines in Fig. 2 represent Eq. (1) with A and B adjusted using the nonlinear least squares method. The best fitting parameters are listed in Table I along with those calculated as described above. Theoretical and experimental values of A are plotted as a function of x in Fig. 3. As can be seen, theory and experiment agree well within a multiplicative factor of 2.88 and scale properly through the different values of x. The agreement is quite satisfactory, taking into account the following approximations introduced in the calculation.

(i) The values of c_{44} used in the calculation of the velocity of sound were taken from measurements performed in nonmixed crystals free from *F* centers. We adopted a linear interpolation between the extreme values of x considering the smooth behavior of mixed crystals phonon dispersion relations at large wavelengths.[12]

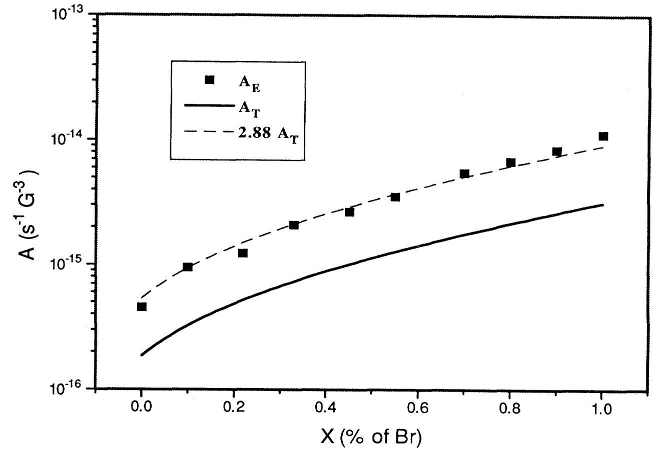

FIG. 3. Experimental (A_E) and theoretical (A_T) dependence on x of the coefficient A in Eq. (1).

(ii) As pointed out in Ref. 7, on the computation of $\nabla|\varphi|^2$, the overlap of orbitals at neighboring ions was underestimated and thus the *F* electron density becomes independent of the relative motion of ions leading to an electron nuclei interaction lower than that which actually exists.

(iii) Only first and second coordinate shells are considered. The contribution from the third shell is negligible in all cases and constituted of the same ions. The fourth shell is more important than the third for the dependence with concentration but its contribution is much smaller than those from the first and second.

CONCLUSIONS

It seems clear that the main mechanism for spin-lattice relaxation for *F* centers in low concentration in mixed alkali halides for magnetic fields between 0.5 and 2.5 T is phonon modulation of hyperfine interaction. The model developed and adapted here applies satisfactorily.

The experimental equipment is appropriate for relaxation measurement from minutes to milliseconds. The optical absorption band seems to be homogeneously broadened and no preferential configuration is seen.

It would be interesting to further check these conclusions measuring T_1 vs H and its dependence on x for other matrices, particularly solid solutions of the same halide and distinct alkalis such as KCl-NaCl. In such cases, a stronger dependence on x is expected.

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[1] J. J. Markham, in *Solid State Physics: Advances in Research and Applications,* edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Suppl. 8.

[2] J. H. Shulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1962).

[3] W. B. Fowler, *Physics of Color Centers* (Academic, New York, 1968).

[4] C. D. Jeffries, Phys. Rev. Lett. **19**, 1221 (1967).

[5] M. C. Terrile, H. C. Panepucci, and R. A. Carvalho, Phys. Rev. B **15**, 1110 (1977).

[6] R. A. Carvalho, M. C. Terrile, and H. C. Panepucci, Phys. Rev. B **15**, 1116 (1977).

[7] H. C. Panepucci and L. F. Mollenauer, Phys. Rev. **178**, 589 (1969).

[8] M. C. Terrile, H. Panepucci, and J. S. Helman, Nuovo Cimento **53**, 446 (1979).

[9] H. Seidel, Z. Phys. **165**, 218 (1961).

[10] B. S. Gourary and F. J. Adrian, in *Solid State Physics: Advances in Research and Applications,* edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 10, p. 127.

[11] P.-O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[12] N. E. Massa, Ph.D. thesis, Vanderbilt University, 1978.

[13] J. T. Lewis, A. Rehoesky, and C. V. Briscol, Phys. Rev. **161**, 877 (1977).

[14] A. Smakula, N. Maynard, and A. Repucci, J. Appl. Phys. **33**, Suppl. 1, 453 (1962).