single tunneling barrier is[6,8] $\delta\varphi_{\max} \approx d/\xi(T)$, we have $j_{\max}/j_2(0) \approx d/\xi(T) \ll 1$. Therefore, we may expand the square roots in Eqs. (5) and keep only the first order term in j^2. In the case $\Delta \gg \omega$, the change $\delta\sigma_2$ due to dc current flow, normalized to the value σ_2^0 of the reactive part of the conductivity at $T=0°\text{K}$ and $j=0$, is given by

$$\delta\sigma_2/\sigma_2^0 = -\tfrac{1}{2}(j/j_2^0(0))^2[(\Delta/\Delta_0)\tanh\tfrac{1}{2}\beta\Delta]^{-1}, \qquad (6)$$

where Δ_0 is the energy gap at $T=0$ and $j_2^0(0)=\frac{1}{2}\pi\Delta_0\sigma_0$. A similar expression can be obtained for $\delta\sigma_1$. The nonlinearity given in Eq. (6) is due to the finite change in the magnitude of the phase of the energy gap across the tunneling barriers. Existing theories of granular superconductors[6,8] predict that the change in the conductivity due to pair breaking[16] is $\delta\sigma_2/\sigma_2^0 \sim -(j/j_{\max})^2$, which, for a given current, is larger than that given by Eq. (6) by a factor of order $\xi_0 l_{\text{eff}}/d^2 \gg 1$ (ξ_0 is the Pippard coherence length). Thus, according to theory, we once again have the result that tunneling is indistinguishable from scattering by point impurities. It should be pointed out, however, that existing theories require that the individual grains become normal at currents above $j_{\max}$. It is possible that the individual grains merely decouple above $j_{\max}$ and that a nonzero energy gap exists in each grain. In that case, the above conclusion regarding the magnitude of $\delta\sigma_2/\sigma_2^0$ may require reexamination.

The microwave transmission at $j=0$ has been measured[10] at 20 GHz as a function of temperature on granular Al films which were evaporated in an oxygen atmosphere. Typically, these films have the following properties: $T_c=2.8°K$, a mean free path $l_{\text{eff}} \approx 5$ Å, average grain size $d \approx 50$ Å ($\tau \approx 0.1$) and a resistivity which increased by about 1% in cooling from room temperature to 4.2 K. The granular structure, the small mean free path, and negative temperature coefficient of resistance, indicate that the conduction mechanism was tunneling between grains. The agreement between the experimental results and that predicted by the Mattis and Bardeen conductivities (Eqs. (5) with $j=0$) is excellent.

We gratefully thank R. V. D'Aiello for communicating his results before publication. We also thank R. Klein for helpful discussions.

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[16] J. Gittleman, B. Rosenblum, T. E. Seidel, and A. W. Wicklund, Phys. Rev. **137**, A527 (1965). The authors employed a theory of Parmenter [R. H. Parmenter, RCA Rev. **23**, 323 (1962)] to calculate the change in σ_2 due to a dc current.

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Modified Orbach Relaxation Process in a La(Cl, Br)$_3$ Matrix*

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We have studied the spin-lattice relaxation rates of cerium and erbium in matrices of La$(1-x\ \text{Cl},\ x\ \text{Br})_3$. The substitution of Br$^-$ for Cl$^-$ in LaCl$_3$ was a technique for artificially introducing random local strains at the sites of paramagnetic impurities. The purpose was to test our earlier proposal that naturally occurring random strains were responsible for the frequent and sometimes large ($\approx 15\%$) discrepancies between the excited-state energy levels as measured by optical techniques and by spin-lattice relaxation. Our model assumes that the variation from site to site of Δ, the first-excited-state energy of the paramagnetic ion, can be described by a Gaussian distribution, with a standard deviation σ, centered at the optically determined value. From our relaxation data we extract the value of σ^2 for each sample. We observe the theoretically predicted modifications to the temperature dependence of the Orbach relaxation mechanism as σ^2 changes with the degree of Br$^-$ substitution. Additional infrared and optical data, taken by other investigators on these samples, are briefly presented. These measurements give the actual distributions in Δ, and the widths are found to be in excellent agreement with the values of 2σ inferred from our relaxation data.

I. INTRODUCTION

THIS paper describes a series of measurements on the electron spin-lattice relaxation rates of trivalent cerium and erbium ions incorporated into a matrix of La$(1-x\ \text{Cl},\ x\ \text{Br})_3$. The purpose was to provide clearer evidence for the modification in the temperature dependence of the Orbach relaxation rate that should occur when there is a variation of the energy levels from one paramagnetic site to another throughout the sample.[1] The degree of modification is dependent upon the amount of variation that occurs in the pertinent energy level and this variation in turn is dependent upon the random local strain. There is a local strain associated with the substitution of Br$^-$ for Cl$^-$ in the LaCl$_3$ lattice and therefore the use of these especially mixed crystals enables one to control the variation of the energy level and hence the modification of the Orbach relaxation rate. These particular paramagnetic systems were chosen for the following reasons: (1) Their spin-lattice relaxation is dominated by an Orbach process over a

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[1] B. A. Young and H. J. Stapleton, Phys. Letters **21**, 498 (1966).

wide temperature range below 4.2°K. (2) They exhibit some evidence of a modified Orbach relaxation process even in the absence of any Br^- doping. (3) They lend themselves to optical or infrared measurements that can be used to complement the relaxation data.

Section II contains a brief outline of the modification of the temperature dependence of the Orbach relaxation rate. In Sec. III, the experimental techniques and results are presented and quantitatively discussed with respect to the Orbach relaxation mechanism. Section IV contains a qualitative explanation of other changes observed in the paramagnetic resonance and relaxation of Ce in these mixed crystals. Supporting results of other investigators using infrared and optical techniques to determine the distribution of excited energy levels in these salts, are briefly discussed in Sec. V. A summary of the results and final comments are made in Sec. VI.

II. THEORY

An examination of data from optical measurements and electron spin-lattice relaxation rates of rare-earth ions indicates that the two techniques often yield widely varying values of Δ, the energy difference between the first-excited crystal-field state and the ground state. This quantity Δ appears explicitly in the temperature dependence of the Orbach relaxation process as[2]

$$1/T_{1O}=B\exp(-\Delta/kT)=B'\Delta^3\exp(-\Delta/kT), \quad (1)$$

where B' is independent of Δ and $\Delta \gg kT$. The values of Δ reported from relaxation data are invariably less than the optical values, whenever a significant discrepancy exists. Reference 1 contains several examples of these discrepancies but one of the most convincing cases is $LaCl_3$ weakly doped ($\approx$1 at.%) with Ce^{3+}. Relaxation measurements by two independent groups[3,4] were made prior to the existence of any optical data and their results both yield a value for Δ of 46°K with an error of ±3°K.[3] Two later independent optical measurements on crystals with similarly weak Ce^{3+} dopings yield Δ values of 55.1°K [5] and 53.1±4.5°K.[6]

In the analysis of their spin-lattice relaxation data, Mangum and Hudson[4] suggested that the observed nonexponential signal recoveries and the deviations of Δ from the optical value, might arise from a distribution of Δ values among the ions in the samples. Young and Stapleton[1] quantitatively amplified this idea by considering a Gaussian distribution of Δ values, centered about $\tilde{\Delta}$ the optical value, with a standard deviation σ. If we restrict ourselves to Kramers' ions, a rather wide distribution of Δ values will not excessively broaden the electron spin resonance (ESR) of the ground doublet since the latter is influenced only by changes in the g tensor that are generally second-order effects. If it is correct to assume that each ion relaxes to the lattice via an Orbach mechanism that is determined by its particular value of Δ according to Eq. (1) and that the total spin system possesses a spin-spin interaction that tends to establish an internal equilibrium within the spin system as it relaxes to the lattice, then the asymptotic relaxation rate, near the end of the recovery, should be[1]

$$1/T_{1O}=B'(2\pi\sigma^2)^{-1/2}\int_0^\infty \Delta^3\exp[-\Delta/kT] \times\exp[-(\Delta-\tilde{\Delta})^2/2\sigma^2]d\Delta. \quad (2)$$

If $\tilde{\Delta}-\sigma^2/kT$ is much greater than σ, then Eq. (2) becomes

$$1/T_{1O}=B'\Delta'^3[1+3(\sigma/\Delta')^2]\exp\left[-\frac{\tilde{\Delta}}{kT}+\frac{\sigma^2}{2(kT)^2}\right], \quad (3)$$

where Δ' is $\tilde{\Delta}-\sigma^2/kT$ and the slope of $\ln T_{1O}$ versus $1/kT$ is

$$\frac{d(\ln T_{1O})}{d(1/kT)}=\tilde{\Delta}+\frac{3\sigma^2(\Delta'+\sigma^2)}{(\Delta'^3+3\sigma^2\Delta')}-\frac{\sigma^2}{kT}. \quad (4)$$

For small values of σ^2/kT Eqs. (3, and 4) become

$$1/T_{1O}\approx B'\tilde{\Delta}^3\left[1-\frac{3\sigma^2}{\tilde{\Delta}kT}\right]\exp\left[-\frac{\tilde{\Delta}}{kT}+\frac{\sigma^2}{2(kT)^2}\right], \quad (5)$$

and

$$\frac{d(\ln T_{1O})}{d(1/kT)}\equiv\Delta_{\text{eff}}\approx\tilde{\Delta}+\frac{3\sigma^2}{\Delta}-\frac{\sigma^2}{kT}. \quad (6)$$

Thus the effect of a nonzero σ is to produce an effective splitting (Δ_{eff}) that is lower than the optical value and is slightly temperature-dependent. Since the temperature dependence of Δ_{eff} is largely masked by the overriding temperature dependence of the total relaxation rate, we consider the reported values of Δ from relaxation measurements to be the average of Δ_{eff} over the limited temperature range of the observed Orbach relaxation rate.

III. EXPERIMENTAL

A. Samples and Apparatus

Single crystals of anhydrous $LaCl_3$ doped with Ce^{3+} or Er^{3+}, and varying amounts of Br^- were prepared and grown from the melt by techniques described by Mikkelson and Stapleton.[3] $LaCl_3$ and $LaBr_3$ were prepared from La_2O_3(99.997% rare-earth purity) by reaction with the appropriate reagent grade acid. $CeCl_3$ with a rare-earth purity of 99.9% and an unknown, but large, ($\geq$45%) cerium oxide impurity was used as the cerium doping agent and in the preparation of $CeBr_3$ via an intermediate carbonate precipitate. $ErCl_3$ and $ErBr_3$ were both prepared directly from the oxide of

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[2] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

[3] R. C. Mikkelson and H. J. Stapleton, Phys. Rev. **140**, A1968 (1965).

[4] B. W. Mangum and R. P. Hudson, J. Chem. Phys. **44**, 704 (1966).

[5] F. Varsanyi and B. Toth, Bull. Am. Phys. Soc. **11**, 242 (1966).

[6] K. H. Hellwege, E. Orlich, and G. Schaack, Physik Kondensierten Materie **4**, 196 (1965).

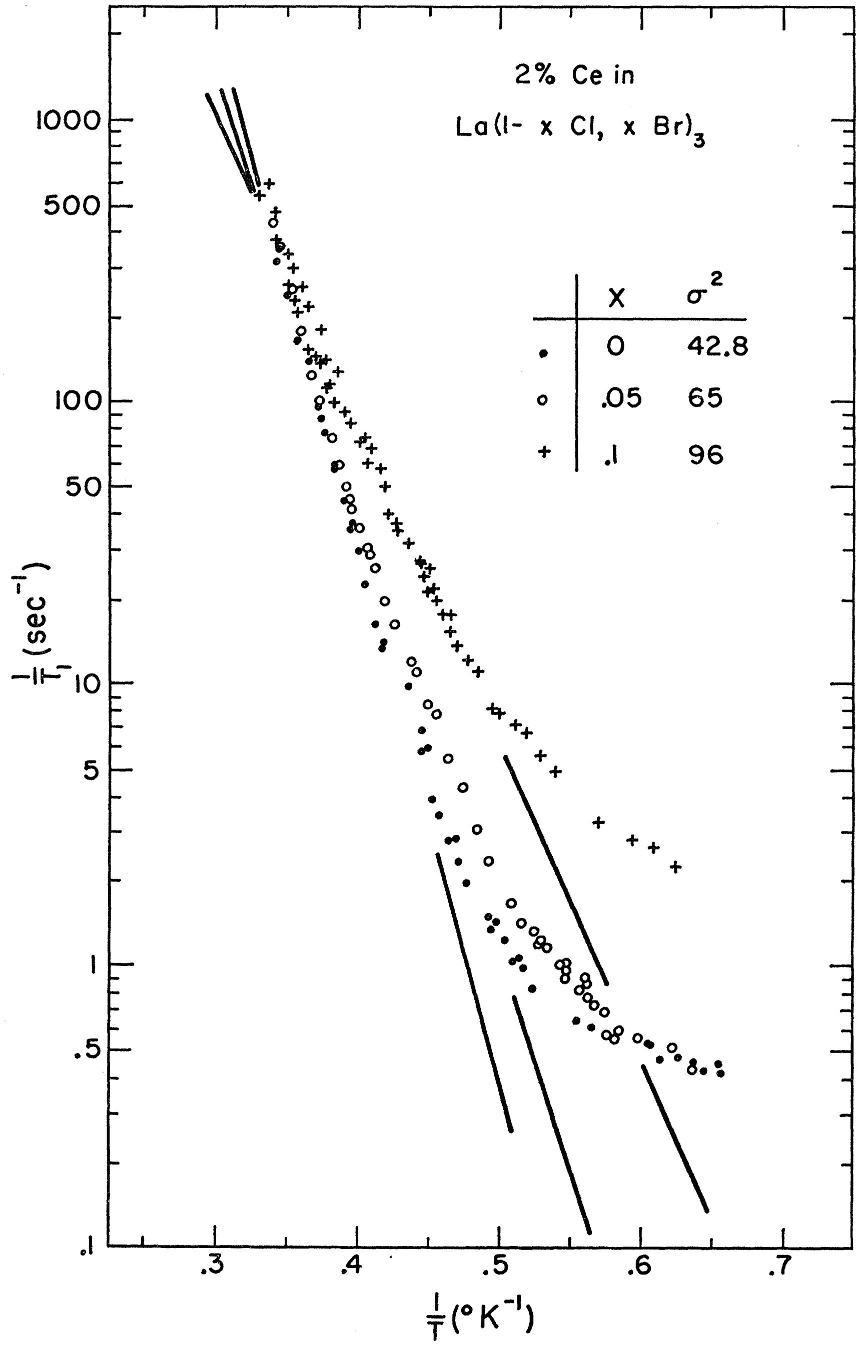

FIG. 1. Temperature dependence of the relaxation rate for 2% Ce^{3+} in mixed $La(Cl, Br)_3$ crystals containing 0, 5, and 10 at.% Br^-. The slopes of the straight lines are approximations to $-\Delta_{eff}$ defined by Eq. (6) of the text. At the lower temperatures, the direct relaxation rate becomes noticeable. As predicted by the theory, the deviation of the data from a straight line at the higher temperatures is greater for larger values of the parameter σ^2. The units of σ^2 are (°K^2) where σ is the standard deviation of an assumed Gaussian distribution of Δ values about an optical value of $\Delta = 54.5$°K. The best-fitting values of all the relaxation-rate parameters are listed in Table I.

enriched Er^{170} (98–99% even-even). The enriched oxide was necessary in order to avoid complications in the relaxation process because of an Er^{167} hyperfine line overlapping the main Er line.

The salt mixtures were dehydrated, purified of nonvolatile impurities such as rare-earth oxides and oxyhalides by sublimation, and passed through a growing furnace. The approximate dopings listed in this paper refer to the composition of the hydrated starting mixtures and neglect the unknown cerium oxide contamination and further purification that takes place during the crystal growth due to zone refining. The latter effect is most evident in the growth of the colored Er-doped samples.

The microwave equipment consisted of a reflection spectrometer using superheterodyne detection, a 600 mW Varian V-58 klystron, a Varian X-13 local oscillator, two Philco 1N3482, and one Arra X110 microwave switching diodes, an LEL (XFT series) 60-MHz balanced mixer and preamplifier and an LEL IF303D50 post amplifier. The microwave power level was increased about 45 dB during the saturating pulse and the low monitor power level required was obtained by a variable attenuator in the monitoring microwave power line that was parallel to a pulse microwave power line. The cavity, which was open to the liquid-helium bath, resonated in a cylindrical TE_{111} mode with a vertical symmetry axis. Both the frequency of the cavity resonance and the coupling to it could be varied while the cavity was in the helium bath. The operating frequency was typically 9.22 GHz.

The temperature of the helium bath was controlled by pumping on it through a Cartesian manostat and the cavity temperature was measured using a carbon resistor in a 250-Hz ac bridge. The observed resistance was corrected for effects due to temperature cycling and magnetic fields, and the result was a temperature accuracy of about ±0.01°K. Measurements of the relaxation rate were made at temperature intervals of about 0.05°K. These rates were measured by viewing the signal recovery versus a variable exponential time sweep on a Tektronix 535A oscilloscope with a type *H* plug-in, or by photographing the recovery against a linear time sweep.

The temperature dependence of the relaxation rates was computer fitted, by the method of least squares, to a sum of direct, modified Orbach, and Raman relaxation processes. The fitting program was such that the exact expression given by Eq. (2) could be used if necessitated by large values of σ^2.

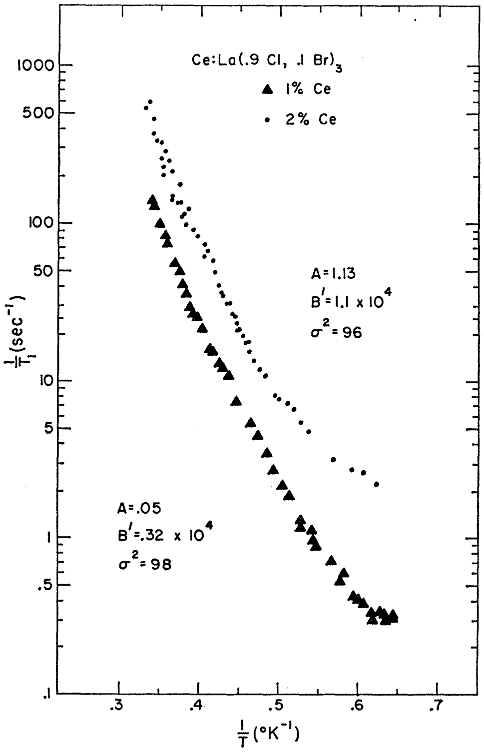

FIG. 2. Temperature and concentration dependence of the relaxation rate for Ce^{3+} in La (0.90 Cl, 0.10 Br)$_3$. A is the direct process coefficient while B' and σ^2 are parameters in Eq. (2) of the text relating to the observed behavior of the Orbach relaxation process. σ^2 is seen to be independent of the Ce-doping while A and B' are strongly dependent upon it. The units of A, B' and σ^2 are (°K^{-1} sec^{-1}), (°K^{-3} sec^{-1}), and (°K^2), respectively.

TABLE I. Best-fitting parameters to the relaxation rate $(1/T_1)$ of Ce-doped mixed crystals of La(Cl, Br)$_3$. The first column indicates the Ce^{3+} doping in at.% and the second column gives the Br^- doping in at.%. The A parameter is a measure of the strength of the direct relaxation rate (AT) while B' and σ^2 are parameters in Eq. (2) of the text, which together with the optically determined splitting $\tilde{\Delta}$ of 54.5°K determine the strength of the Orbach relaxation rate.

Ce in La(Cl, Br)$_3$ at.% Ce^{3+}	at.% Br^-	A (°K^{-1} sec^{-1})	B' (10^4 °K^{-3} sec^{-1})	σ^2 (°K^2)
2%	0%	0.282±0.005	4.68±0.28	42.8±1.1
2%	0%[a]	0.272±0.007	2.61±0.23	50.0±1.5
2%	5%	0.261±0.013	2.17±0.14	65.0±1.2
2%	10%	1.13±0.07	1.07±0.09	96.2±2.0
1%	10%	0.054±0.013	0.318±0.024	98.5±1.9

[a] Samples tabulated in the first two rows are the same, but the data of the second row were taken after the sample was neutron irradiated in a flux of 10^{13} n/cm^2 sec for 1 h.

B. Orbach Relaxation Rate of Cerium

Figure 1 shows the temperature dependence of the asymptotic spin-lattice relaxation rate near thermal equilibrium for 2% Ce^{3+} in various mixed crystals of La(Cl, Br)$_3$ with the external magnetic field parallel to the crystal axis. As the percentage of Br^- was changed through 0, 5, and 10%, the best fitting values of σ^2 increased from 42.8 to 65, and 96°K^2 ($2\sigma=9.1$, 11.2, and 13.6 cm^{-1}) corresponding to progressively smaller Δ_{eff} values that are roughly indicated in Fig. 1 by straight lines. Furthermore, the temperature variation of Δ_{eff} becomes more distinct as the Br^- concentration is increased because the straight line becomes a poorer approximation to Eq. (6). In fitting these relaxation data, an optical value of 54.5 was assumed for $\tilde{\Delta}$ and no Raman term was required to improve the fit to the theoretical rate. The direct process coefficient A and the two Orbach parameters B' and σ^2 are listed in Table I for the various Ce-doped samples.

The nature of the signal recovery after saturation was altered as the Br^- concentration was increased. With no Br^-, the recovery of the Ce spin-resonance signal was essentially exponential over the entire recovery. With 5% Br^-, the initial 20% of the recovery was faster than the remaining portion, and with 10% Br^- this initial period of rapid change extended up to 30–50% of the total recovery. All rates reported here are asymptotic limits near the end of the recovery. We attribute this increase in the nonexponential character of the signal recovery to a diminished spin-spin interaction between ions in the ground doublet as it is inhomogeneously broadened with increased Br^- concentration. While the simple theory developed thus far relies on a spin-spin interaction to bring about internal equilibrium to the spin system, the quantitative results of this interaction have been neglected. Table I shows that B' systematically decreases as σ^2 increases while our simple theory predicts that B' will be constant. It should be noted that

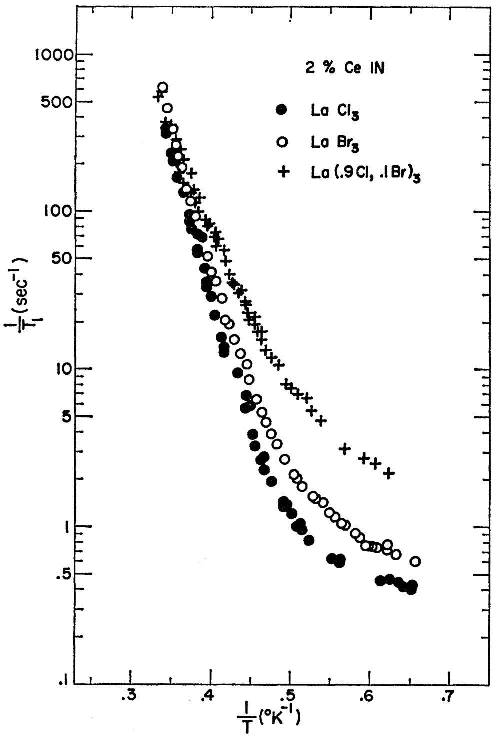

FIG. 3. Temperature dependence of the relaxation rate for 2% Ce^{3+} in $LaCl_3$, $LaBr_3$, and La (0.90 Cl, 0.10 Br)$_3$. The displacement of the points for the mixed crystal indicates that its rate is not simply some average of the two pure crystal rates.

these two fitting parameters σ^2 and B' can be determined almost independently since only σ^2 determines the slope of $\ln(1/T_1)$ versus $1/T$. If the diminishing values of B' do reflect a decreasing spin-spin interaction, the same qualitative effect should occur if we reduce the cerium concentration. Figure 2 and Table I show a comparison of Ce relaxation rates in La (0.90 Cl, 0.10 Br)$_3$ for 2% and 1% Ce dopings with the external field parallel to the crystal axis. As far as the Orbach process is concerned, σ^2 remains essentially constant (96 versus 98°K^2) indicating that the local strains are not dependent upon the Ce concentration, but B' drops by a factor of 3.4 as the Ce concentration is decreased by a factor of 2.

A sample of 2% Ce in $LaBr_3$ was examined with the external field parallel to the crystal axis, and the data are compared in Fig. 3 with the results of 2% Ce in $LaCl_3$ and La (0.90 Cl, 0.10 Br)$_3$. This shows that the Orbach relaxation rate in the mixed crystal is sufficiently different from either the rate in the trichloride or the tribromide so that some sort of mixture of rates can be ruled out. Unfortunately, the optical value of $\tilde{\Delta}$ in the tribromide has not been reported and our computer program cannot fit both $\tilde{\Delta}$ and σ^2 simultaneously, since they both alter the same features of the rate in a very interdependent manner.

The sample composed of 2% Ce in $LaCl_3$ was bombarded with fast neutrons in a flux of 10^{13} n/cm^2 sec for 1 h in order to observe the effect on σ^2. Table I shows that while σ^2 increased by only 17%, B' dropped by a factor of 1.8. The effect of neutron bombardment was thus to change B', possibly by affecting the phonon spectrum, and to keep both A and σ^2 approximately constant.

C. Orbach Relaxation Rate of Erbium

Here again we attempted to induce a broadening in the first-excited state of Er^{3+} in $LaCl_3$ by Br^- substitution and neutron bombardment. It should be noted, however, that the relaxation data of Mangum and Hudson[4] suggest that a large broadening can sometimes be introduced during the ordinary growth of Er-doped $LaCl_3$ since their reported Δ values vary among samples from 48.9° to 54.5°K, the latter being the optical value.[7]

The ESR absorption linewidth increased rapidly with increasing Br^- concentration. The observed peak-to-peak derivative width of the absorption line for a perpendicularly oriented magnetic field was 1.4 Oe for 0.1% Er in $LaCl_3$, 3.4 Oe for 0.1% Er in La(0.99 Cl, 0.01 Br)$_3$, 9.2 Oe for 1% Er in La(0.97 Cl, 0.03 Br)$_3$, 22 Oe for 1% Er in La(0.94 Cl, 0.06 Br)$_3$, and 150 Oe for 1% Er in La(0.90 Cl, 0.10 Br)$_3$. Neutron bombard-

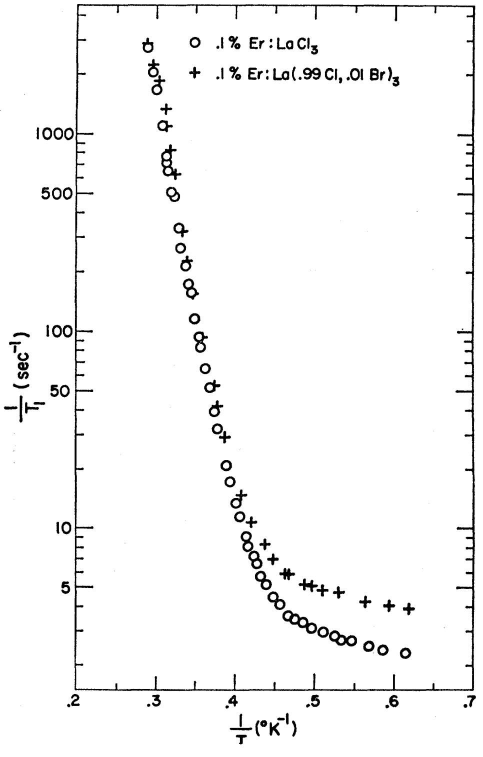

FIG. 4. Temperature dependence of the relaxation rate for 0.1% Er^{170} in $LaCl_3$ and La (0.99 Cl, 0.01 Br)$_3$. The differences in the rates between two samples appear to be caused by uncontrolled differences in the histories of the two samples rather than to strains introduced by the Br^- substitution. The microwave frequencies were 9.24 and 9.22 GHz for the pure and mixed crystals, respectively. The best-fitting values of the relaxation-rate parameters are listed in Table II.

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[7] F. Varsanyi and G. H. Dieke, J. Chem. Phys. 36, 2951 (1962).

TABLE II. Best-fitting parameters to the relaxation rate ($1/T_1$) of Er^{170}-doped mixed crystals of La(Cl, Br)$_3$. The first column indicates the at.% of trivalent Er^{170} and the second column gives the Br$^-$ doping in at.%. The A parameter is a measure of the strength of the direct relaxation rate (AT) while B' and σ^2 are parameters in Eq. (2) of the text, which together with the optically determined splitting $\bar{\Delta}$ of 54.5°K determine the strength of the Orbach relaxation rate. C indicates the strength of the Raman relaxation rate (CT^9).

Er^{3+} at.%	La(Cl, Br)$_3$ Br$^-$ at.%	A (°K^{-1} sec^{-1})	B' (10^4 °K^{-3} sec^{-1})	σ^2 (°K^2)	C (10^{-4} °K^{-9} sec^{-1})
0.1	0	1.38±0.02	7.03±0.04	12.6±1.9	4.78±0.96
0.1	1	2.28±0.07	13.5±2.1	2.0±4.0	9.76±2.68
1	3	2.11±0.05	7.84±0.97	7.1±3.4	14.6±1.7
1	6	2.88±0.12	5.59±0.68	31.0±4.3	11.2±6.2

ment, on the other hand, did not broaden the ESR line at all. The results of relaxation measurements on four of the above samples are given in Figs. 4 and 5 and in Table II. These data suggest that possibly the random local strains introduced during the growth of Er-doped LaCl$_3$ crystals dominate over any effects of small Br$^-$ additions. It is worth noting that pure ErCl$_3$ is monoclinic[8] rather than hexagonal as LaCl$_3$. Alternatively, one could interpret these concentration data as due to a relief from local strains in Er-doped LaCl$_3$ as small amounts of Br$^-$ are added since σ^2 was first reduced, then increased monotonically as the Br$^-$ concentration was increased. Again the values of B' decreased as σ^2 increased in the mixed crystals. The nature of the Er^{3+} signal recoveries was similar to that for the Ce^{3+}. All samples recovered in a fairly exponential manner above 2.8°K, but as the temperature was lowered, they became increasingly nonexponential to a degree that increased with the Br$^-$ concentration. The signal recovery of 0.1% Er^{170} in LaCl$_3$ was perfectly exponential over the entire temperature range, but for 1% Er^{170} in La(0.94 Cl, 0.06 Br)$_3$ at 1.5°K, only the last $\frac{1}{6}$ of the recovery appeared exponential. Pulse durations of 6 msec were more than adequate to saturate the entire absorption line in all the Er samples.

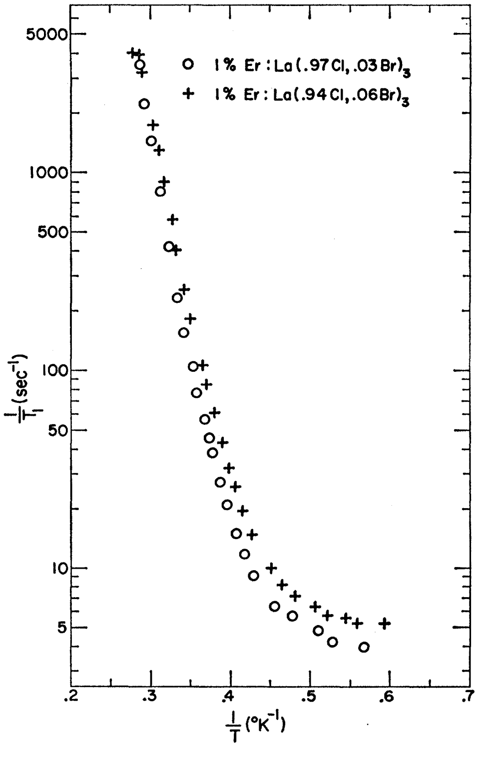

FIG. 5. Temperature dependence of the relaxation rate for 1% Er^{170} in La (0.97 Cl, 0.03 Br)$_3$ and La (0.94 Cl, 0.06 Br)$_3$. The parameters of the relaxation rate changed for these samples in the same way as those of the Ce-doped mixed crystals when the Br$^-$ concentration was increased. Both samples were examined at 9.25 GHz and the best-fitting values of the relaxation-rate parameters are listed in Table II.

IV. CERIUM DIRECT RELAXATION AND LINE SHAPE

The data of Fig. 1 and Table I show that the direct relaxation rate of Ce^{3+} is modified in these mixed crystals. Figure 6 shows a comparison in the angular dependence of the direct process coefficient $A(\theta)$ for 2% Ce in La(0.90 Cl, 0.10 Br)$_3$ and 1% Ce in LaCl$_3$. The latter data are from Mikkelson and Stapleton[3] who observed no change when the concentration was increased to 2%. As Table I indicates, we did observe a Ce concentration dependence in $A(0°)$ for our mixed crystals. The data for the mixed crystal in Fig. 6 was obtained by subtracting the isotropic Orbach contribution from the angular-dependent total relaxation rate at 1.6°K. The isotropy of the Orbach process was verified to within 10% by angular measurements at 2.6°K over the range from $\theta=0°$ to $\theta=60°$. Another feature related to the modification of the direct process (which is dependent upon both the field direction and magnitude) was an increase in $g_\perp$. With the magnetic field at 84° from the symmetry axis, the Ce^{3+} absorption line in La(0.90 Cl, 0.10 Br)$_3$ was centered at 9.1 rather than at 14.4 kOe, its position in the unmixed crystal.

A qualitative explanation of the changes in $A(\theta)$ and $g_\perp$ can be given in terms of random local strains due to the presence of the Br$^-$ impurities. The single $4f$ electron in Ce^{3+} produces two J levels about 2300 cm^{-1} apart with the $J=\frac{5}{2}$ level lower. The symmetry of the crystal field about the Ce^{3+} ion in unstrained LaCl$_3$ or LaBr$_3$ is C_{3h}, which means that only the tensor operators

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[8] R. W. Wykoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1957), Vol. II, Chap. V, p. 64.

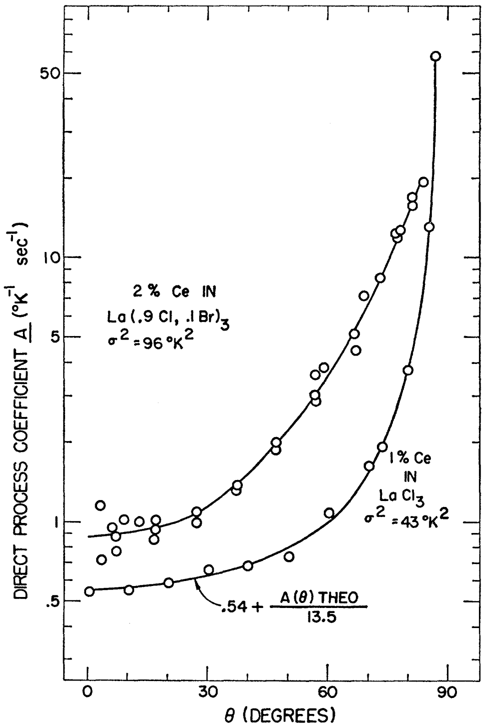

FIG. 6. Angular dependence of the direct process relaxation coefficient $A(\theta)$ for 2% Ce in La (0.90 Cl, 0.10 Br)$_3$ compared with similar data for 1% Ce in LaCl$_3$. The latter data and theoretical curve were taken from, and are more fully discussed in Ref. 3. θ is the angle between the applied magnetic field and the crystal symmetry axis.

T_n^m with $n=2$, 4, 6 and $m=0$, ±6 couple the various basis states $|J, J_z\rangle$ in the Hamiltonian of the crystal field. It is useful to consider the problem under various approximations.

1. *Neglect of the upper* ($J=\frac{7}{2}$) *manifold and strain effects.* The $J=\frac{5}{2}$ level is split by the crystal field of C_{3h} symmetry into three Kramers' doublets described in order of increasing energy by $J_z=\pm\frac{5}{2}$, $\pm\frac{1}{2}$, and $\pm\frac{3}{2}$. Theoretically the g values for the lowest doublet are then $g_{\|}=30/7\approx4.3$ and $g_{\perp}=0$. Although paramagnetic relaxation would occur, no ESR signal could be observed since $g_{\perp}=0$. The application of a magnetic field at an H at an angle θ with respect to the crystal symmetry axis, will admix the various states and break the time-conjugate nature of the ground doublet through the Zeeman interaction.

$$\mathcal{H}_z=\beta\Lambda\mathbf{H}\cdot\mathbf{J}=\beta\Lambda H(J_z\cos\theta+J_x\sin\theta), \qquad (7)$$

where Λ is the Landé g value, and the axes are chosen so that H_y is zero. Under our present approximation J_z cannot couple any states and, as a result, $A(\theta=0°)$ will be zero. As the direction of the magnetic field is moved away from the crystal axis, J_x will couple the nearby doublets (≤100 cm^{-1} away) into the ground states and $A(\theta)$ will increase from zero.

2. *Neglect of strain effects only.* By taking into account the admixture, through the static crystal-field interaction, of the much higher $J=\frac{7}{2}$ manifold into the ground doublet, one calculates, using reasonably accurate crystal-field parameters,[3,5,6] a $g_{\|}$ that is slightly lower than 30/7 and a $g_{\perp}$ that is around 0.1. Thus one obtains a closer agreement with the measured g values of 4.0366 and 0.17 ± 0.08, respectively.[9] $A(0°)$ will no longer be zero since $|J=\frac{7}{2}, J_z=\pm\frac{5}{2}\rangle$ states are admixed into the ground doublet through the J_z operator in the Zeeman Hamiltonian. The value of $A(0°)$ can be estimated using the theoretical approach of Orbach[2] and the result is of the order of 10^{-3} sec^{-1} °K^{-1}, whereas the experimental value in LaCl$_3$ is about 0.5 sec^{-1} °K^{-1}. As θ is increased, the effects of magnetic admixtures from within the $J=\frac{5}{2}$ manifold soon dominate. As seen in Fig. 6, $A(\theta)$ increases to 50 sec^{-1} °K^{-1} near 90°, in close proportional agreement with the theory.

3. *Inclusion of strain effects but neglect of the* $J=\frac{7}{2}$ *manifold.* Local strains will reduce the symmetry from C_{3h} and permit both $A(0°)$ and $g_{\perp}$ to be nonzero even if the $J=\frac{7}{2}$ manifold is ignored. In addition to the previously mentioned increase of $g_{\perp}$ in the La(0.90 Cl, 0.10 Br)$_3$ crystal, the cerium resonance also displayed an extreme asymmetry at the low values of θ, which

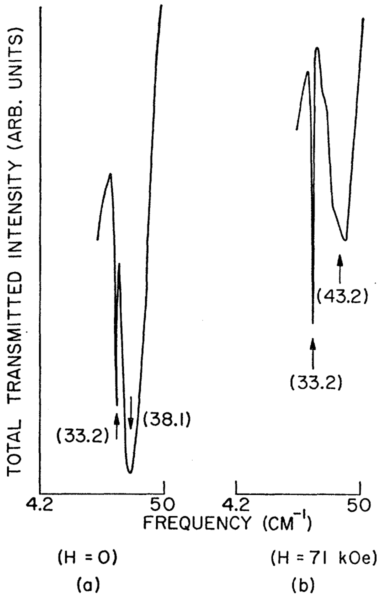

FIG. 7. Infrared absorption spectrum of 2% Ce in LaCl$_3$ in (a) zero magnetic field; and (b) 71 kOe, as measured by R. G. Wheeler (see Ref. 10) using Fourier transform spectroscopy. These unnormalized total intensity measurements were made near 1°K with the light propagation vector and H both parallel to the crystal axis. The resolution of the instrument is 0.5 cm^{-1}. The extremely narrow, field-independent line at 33.2 cm^{-1} is associated with the cerium impurity, but its origin is not understood. The broad line is due to a transition between the lowest doublets.

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[9] C. A. Hutchison, Jr., and E. Wong, J. Chem. Phys. **29**, 754 (1958).

indicated a smearing of the resonance toward higher fields. This is to be expected on the basis of local strains since any admixed wave function will reduce the value of $g_{\parallel}$ for the ground doublet. No structure was observed on the line, and its shape became more symmetric, but wider, at larger angles.

The data of Fig. 6 suggest that the discrepancy between theory and experiment for $A(0°)$ is probably because of the presence of these local strains, since the discrepancy is made even larger with a Br$^-$ doping. A detailed comparison between theory and experiment for $A(\theta)$ at larger angles is given in Ref. (3).

V. INFRARED AND OPTICAL MEASUREMENTS

Shown in Fig. 7 is an infrared spectrum for 2% Ce in LaCl$_3$ as measured by Wheeler[10] using Fourier transform spectroscopy. The approximate zero-field positions of the broad line at 38.1 cm^{-1} (54.8°K) is in good agreement with optically determined values of Δ, and the field dependence implies an effective g value of about 1.54 for this transition. The values of $g_{\parallel}$, as measured by electron spin resonance in the ground doublet, and calculated theoretically for the first excited doublet, are 4.037 [9] and 0.857, [3] respectively, yielding effective $g_{\parallel}$ values of 2.45 or 1.59 for the infrared transition. The width of the broad line in zero magnetic field is in reasonable agreement with a value of $2\sigma = 9.1$ cm^{-1} obtained from our relaxation data on a crystal of the same composition. The exceedingly narrow (instrument limited) line at 33.2 cm^{-1} (47.7°K) is within the error of relaxation measurements of $\Delta = 46 \pm 3$°K [3,4] for Ce in LaCl$_3$ when any distribution of excited-state energies is ignored. Because this line does not shift with magnetic field and because even lower values of Δ can be obtained from relaxation measurements by incorporating Br$^-$ into the lattice, we consider this agreement fortuitous, but we are unable to explain the presence of this line.

Optical studies on our Er-doped La(Cl, Br)$_3$ samples were made by Varsanyi.[11] Using fluorescence techniques, he compared the linwidth of a transition from a metastable fluorescent level down to the first excited state (at an energy Δ above the ground state) in 0.5% Er-doped LaCl$_3$ and two of our samples containing 1% Er in La(0.97 Cl, 0.03 Br)$_3$ and La(0.94 Cl, 0.06 Br)$_3$. In the sample that contained no Br$^-$, the fluorescence line had a width of about 0.3 cm^{-1}. In both of the Br$^-$-doped samples, the same transition was of the order of 10 cm^{-1} wide but the 6% Br$^-$-doped crystal exhibited the wider line shape. These broadened lines had a resolvable structure (2 or 3 distinct features) and were asymmetric with a tail on the high-energy side. The approximate width of the absorption line due to a transition from the ground state to the metastable fluorescent state in these samples was 1 cm^{-1}. Thus the broadening of these optical transitions due to the addition of Br$^-$ appears primarily because of a broadening of the first excited state and is in qualitative agreement with our relaxation data.

VI. SUMMARY

We have presented some of the details of a model that can resolve the discrepancy between the experimental values of Δ, the first-excited state energy of a paramagnetic ion, as determined by optical methods and by spin-lattice relaxation measurements. The theory rests upon an assumed distribution of Δ values throughout a given sample. By examining relaxation times in various mixed salts of La(Cl, Br)$_3$ containing Ce^{3+} or Er^{3+}, we have observed changes in the temperature dependence of the Orbach relaxation rate consistent with the assumed Gaussian distributions of Δ with different standard deviations σ. Measurements of the actual Δ distributions have been presented from the infrared and optical studies of others on these samples, and the widths of these distributions are in good agreement with the values of 2σ inferred from our relaxation data. We conclude, therefore, that relatively wide ($\approx$10 cm^{-1}) distributions in Δ are responsible for the large ($\leq$15%) differences in the reported values of Δ as measured optically or by spin-lattice relaxation techniques. Furthermore, these experiments show that to rely solely on the use of spin-lattice relaxation techniques in the determination of low-lying energy levels in paramagnetic salts is to risk serious error.

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[10] R. G. Wheeler and co-workers (private communication).

[11] F. Varsanyi (private communication).