Spin-lattice relaxation of trivalent uranium in anhydrous lanthanum trichloride*

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Pulse-saturation, g-shift, and linewidth broadening data are presented for anhydrous lanthanum trichloride containing 0.01-at.% U^{3+}. The microwave frequency was 16.3 GHz. Pulse-saturation data from 1.8 to 7.3 K indicate a Raman relaxation rate which varies faster than T^9 and is anisotropic with respect to magnetic field direction. A temperature-dependent g shift, varying approximately as T^4, is observed between 19 and 29 K for a perpendicular magnetic field orientation. Relaxation-induced line broadening is observed, but only at temperatures above 25 K.

We have measured spin-phonon interactions in a single crystal[1] of $LaCl_3$ containing 0.01-at.% U^{3+}. The measurements were made at 16.3 GHz as a function of temperature and θ, the angle between the magnetic field and the hexagonal crystalline symmetry axis. Included are (i) direct measurements of the spin-lattice relaxation rate $1/T_1$, as obtained from pulse-saturation data between 1.8 and 7.3 K, (ii) indirect measurements of $1/T_1$ as obtained from the relaxation-induced contribution to the linewidth $1/T_2$, between 25 and 29 K, and (iii) measurements of the phonon-induced shift in $g_\perp$ between 19 and 29 K. The spectrometer incorporated a TE_{112} cylindrical microwave cavity which was enclosed in a thermal-isolation can and coupled to the liquid-helium bath with ^4He exchange gas. Details of the spectrometer and the temperature control system have been published elsewhere.[2,3] Lock-in detection was employed for linewidth and g-shift measurements at higher temperatures. All measurements were made on the absorption due to $^{238}U^{3+}$, for which[4] $|g_\parallel| = 4.153 \pm 0.005$ and $|g_\perp| = 1.520 \pm 0.002$.

The sample on which our measurements were made was cut from a larger crystal which had been stored for several years in mineral oil. The sample had no visible defects. Mass-spectroscopic analysis and the electron-spin-resonance spectrum revealed a weak impurity concentration of Nd^{3+}. No other resonances in the spectrum were detected. The rare-earth purity of the La was 99.997%.

The usual functional form[5] for the spin-lattice relaxation rate of a Kramers doublet is

$$1/T_1 = AT + BT^9 + C/(e^{\Delta/kT} - 1), \qquad (1)$$

when the following assumptions are satisfied: (i) the phonon spectrum is isotropic, (ii) the density of phonon states follows a Debye model, (iii) the problem is treated in the low-temperature limit, (iv) there is only one excited doublet with an energy Δ below $k\Theta_D$, the Debye limit, and (v) the Zeeman splitting $h\nu$ is less than kT. A fit of our pulse-saturation data to Eq. (1) for $\theta = 18°$ yields the parameters $A = 0.65 \pm 0.06$ $K^{-1}sec^{-1}$, $B = (6.0 \pm 1.4) \times 10^{-6}$

$K^{-9}sec^{-1}$, $C = (8.5 \pm 1.1) \times 10^6$ sec^{-1}, and $\Delta/k = 66.7 \pm 1.3$ K. These data points, but not the fitting curve, are shown in Fig. 1. A comparison of measurements made during two different experimental runs at the same angle showed that for 24 pairs of data taken within 0.002 K of each other, the rms reproducibility was within 3%.

We do not consider this fit of the data as meaningful for two reasons. First, if the doublet giving rise to the resonant Raman (Orbach) process were
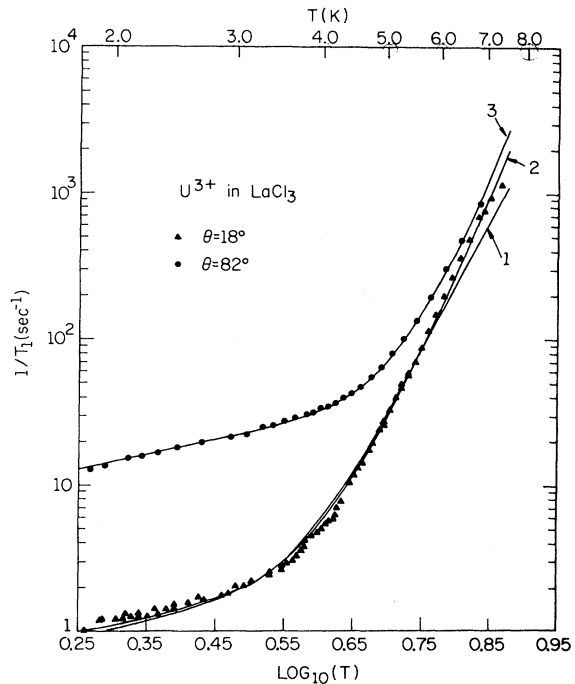

FIG. 1. Pulse-saturation data for the spin-lattice relaxation rate $1/T_1$ of 0.01-at.% U^{3+} in $LaCl_3$ as a function of temperature for two values of the angle θ between the external magnetic field and the crystalline symmetry axis. Curve 1 represents the best fit of the $\theta = 18°$ data to Eq. (2). Curves 2 and 3 represent fits of the data to Eq. (3). The parameters of these latter fits are listed in Table I.

TABLE I. Fitting parameters for the data in Fig. 1 to Eq. (3). The Debye temperature for $LaCl_3$ was taken (see Ref. 10) to be 155 K. The parameter Δ was not allowed to vary in the fitting program; instead, various values of Δ were tried and the value given in the table is that corresponding to a minimum in the variance of the fit.

θ (deg)	A (sec^{-1})	$10^{-9} B'$ (sec^{-1})	Δ/k (K)
82	7.24 ± 0.13	5.30 ± 0.003	156.5
18	0.54 ± 0.10	3.93 ± 0.05	156.5

the only excited doublet, one would expect[6] C/B to be about $15\Delta^{10}/128\pi^7 k^9 \Gamma$ K^9, where Γ is the width of either component of the excited doublet. Our data would imply Γ is about 50 K. This excessive energy width would be reduced by the presence of three additional doublets, but this reduction is unlikely to place Γ below 12 K. Second, U^{3+} ($5f^3$) is the actinide analog of Nd^{3+} ($4f^3$), which has doublets in the $LaCl_3$ lattice[7] with excitation energies of 166, 177, 352, and 359 K. Resonant Raman processes in $LaCl_3$: Nd involving the first two excited states have been reported from linewidth studies[8] which exhibited phonon-induced broadening above 16 K. Such processes have not been observed in pulse-saturation studies of $LaCl_3$: Nd at temperatures below 8 K. We have searched for evidence of a resonant Raman relaxation process in $LaCl_3$: U using linewidth data up to our maxiumum regulated temperature of 29 K. Our linewidth measurements were taken with a perpendicular field orientation where the temperature-independent linewidth was 6.3 Oe. No line broadening was observed until 25 K. Between 25 and 29 K the observed linewidth increased only 2.1 Oe. Such a small change does not allow us to determine the temperature dependence of the dominant relaxation mechanism at this temperature,
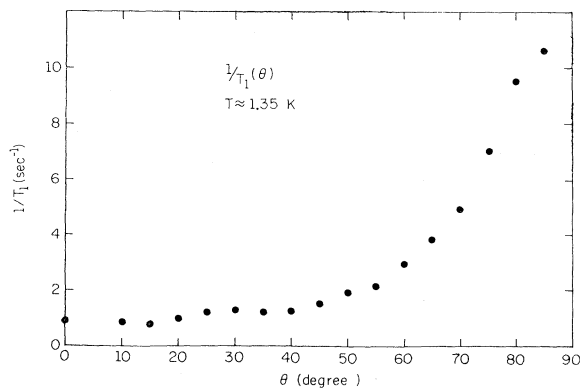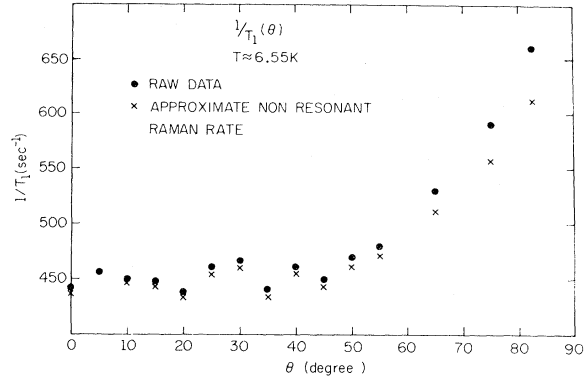

FIG. 3. Relaxation rate of $LaCl_3$: U^{3+} as a function of the angle θ between the external magnetic field and the crystalline symmetry axis at a temperature of about 6.55 K. The circles represent the measured relaxation rates. The crosses are obtained by subtracting the contribution of the direct process as extrapolated from the data in Fig. 2.

but the extreme differences in T_1 between $LaCl_3$:Nd and $LaCl_3$: U lead us to conclude that no resonant Raman processes are present in the latter.

Optical data[9] on $LaCl_3$: U^{3+} exist, but experimental values of the energy levels in the lowest-J manifold are not reported. The Debye temperature Θ_D, of the $LaCl_3$ lattice[10] is 155 K. This can only be considered a crude approximation to the phonon cutoff frequency, however, since phonons with energies of 166 and 177 K must be available to explain the observed resonant Raman process in $LaCl_3$: Nd.

Thus we shall assume that all the excited doublets of $LaCl_3$:U^{3+} lie above $k\Theta_D$ and consider possible consequences to the Raman relaxation rate. With $C = 0$, Eq. (1) becomes

$$1/T_1 = AT + BT^9, \qquad (2)$$

and curve 1 in Fig. 1 represents the best fit of our data at $\theta = 18°$ to this expression. Clearly the fit is poor. If, in the derivation of the Raman rate, one does not neglect the phonon energies $\hbar\omega$ in comparison with the ionic excitation energy Δ, then Eq. (2) becomes

$$\frac{1}{T_1} = AT + B' \int_0^{k\Theta_D/\Delta} \frac{dx\, x^8}{\sinh^2(x\Delta/2kT)(1 - x^2)^2}, \qquad (3)$$

where $x = \hbar\omega/\Delta$ and only the lowest excited doublet at an energy Δ is assumed to contribute appreciably to the relaxation. The results of fits to Eq. (3) are given in Table I and the corresponding curves are shown along with the data in Fig. 1.

A more exact treatment would add to Eq. (3) additional terms for each of the higher doublets, as well as cross terms between the different contributions from each doublet.[11] Without knowledge of the energy levels, this refinement does not seem

FIG. 2. Relaxation rate of $LaCl_3$: U^{3+} as a function of the angle θ between the external magnetic field and the crystalline symmetry axis at a temperature near 1.35 K (as estimated from the vapor pressure of the liquid-helium bath).
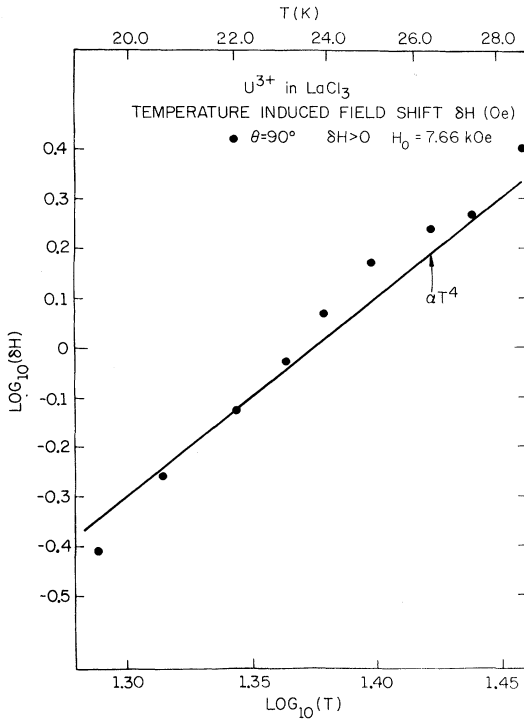
FIG. 4. Phonon-induced shift in the resonant field of $LaCl_3 : U^{3+}$ as a function of temperature with the magnetic field perpendicular to the crystalline symmetry axis. At this orientation the resonant field increased as the temperature increased. H_0 refers to the resonant field of the unshifted resonance line at lower temperatures.

feasible.

The fitting parameter Δ/k in Table I indicates that the upper limit of the intergral in Eq. (3) is nearly unity, and thus the resulting value of the integral is very sensitive to the assumed density of states near the Debye limit. It is unlikely that the Debye model assumed in Eq. (3) is at all appropriate.

A further sophistication would be to include ef-

fects of phonon dispersion. Kiel and Mims, [12] following an approach used by Vredevoe, [13] assumed an isotropic phonon spectrum with dispersion in order to explain their observation of Raman relaxation rates which varied between T^{10} and T^{11}. We do not quite agree with their calculations. [14] In addition, one should consider the proper form of the orbit-lattice interaction in the short-wavelength regime for a Hamiltonian such as that due to Blume and Orbach. [15] Only in the long-wavelength limit do the matrix elements of the strain operator factor into a term depending on temperature and the magnitude of the phonon wave vector times a temperature-independent angular function, thereby simplifying the integration over an assumed spherical Brillouin zone. At higher phonon frequencies this factorization does not occur, and it becomes more judicious to perform the integration over the exact Brillouin zone.

Lacking any phonon spectrum for $LaCl_3$, we have not attempted to fit our data to anything more complex than Eq. (3).

Additional relaxation data were taken as a function of θ at 1.35 and 6.55 K, and are shown in Figs. 2 and 3. Figure 2 shows the strong angular anisotropy of the direct relaxation process, while Fig. 3 indicates an anisotropy in the Raman rate. Others have also reported anisotropic Raman rates in the $LaCl_3$ lattice[8,16] and a model calculation by Stedman and Newman[17] yields qualitative agreement with the experimental data.

Figure 4 shows a temperature-dependent g shift which roughly follows a T^4 dependence, as expected. [18] We were not able to detect a g shift with a parallel orientation of the magnetic field.

In conclusion, we have been able to explain our relaxation data for $LaCl_3 : U^{3+}$ by assuming a direct and a Raman relaxation process, provided that, in computing the latter, we did not neglect the phonon energies with respect to an electronic doublet, which was assumed to have an excitation energy just beyond the phonon cut-off frequency.

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[14]Their Eq. (7) would appear to contain two errors: (i) The v^{-1} outside the integral arises from a term $(\partial\omega/\partial k)^{-1}$ and belongs more properly inside the integral along with the other factors containing dispersion effects; (ii) the proper upper limit on the integral is unclear since an isotropic density of states in k space would imply a limit of $(3\pi^2/4)^{1/3} \approx 0.62\pi$, while the dispersion relation implies a singularity of order 1 in $(\partial\omega/\partial k)^{-1}$ at $\frac{1}{2}\pi$. There-

fore the quantitative aspects of their conclusions will be appreciably altered in the case where phonons of energy comparable to that of the first-excited doublet participate in the relaxation.

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