

cm^{-3} is about 500 \AA , while in InSb with 3×10^{18} donors cm^{-3} it is only 20 \AA . The LO phonon is almost completely shielded in the heavily doped InSb and cannot interact with electrons in the metal.

Disappearance of the oscillation of dI/dV in the presence of a magnetic field can be understood by taking into consideration that several Landau levels lie in the energy interval for one peak and the peak is broadened and becomes small.

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MULTIPHONON ORBIT-LATTICE RELAXATION IN LaBr_3 , LaCl_3 , AND LaF_3 *

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The phenomenon of multiphonon orbit-lattice relaxation has been recognized as a significant mechanism in the decay of excited electronic states of ions in crystals.¹ For the case of rare-earth ions, such transitions are observed between spin-orbit levels which are separated by energies much greater than the Debye energy of the lattice. Transition rates which are of the order of radiative decay rates (typically 10^2 - 10^5 sec^{-1}) can occur for processes involving the emission of as many as seven optical phonons. Although order-of-magnitude estimates have met with moderate success,² these exceedingly complex processes are not amenable to *ab initio* calculations. It is not even certain whether the process arises from the high-order crystalline field terms in first-order perturbation theory or from the harmonic crystalline field terms carried to high orders in the perturbation theory.³ Experimentally, the dependence of fluorescence quenching on the transition energy gap has been observed through excited-state lifetime measurements.^{4,5} Recently, pure multiphonon transition rates have been determined by measurement of both excited-state lifetimes and multiphonon relaxation branching ratios, i.e., relative quantum efficiencies.⁶⁻⁸

These studies have demonstrated, through the temperature dependence of the multiphonon relaxation rates,^{6,7} that the decay generally involves the emission of high-energy optical phonons.⁹ This result is reasonable, in view of recent studies of the vibronic sidebands accompanying sharp electronic transitions in rare earth chlorides.¹⁰ These spectra yield the effective density of phonon states for the ion-lattice interaction,¹¹ and indicate a large number of high-energy optical branches with large densities of states. Since these branches correspond to directions in the Brillouin zone, they have a low point symmetry, and in view of the large number of terminal atomic states available (i.e., all of the Stark levels of the multiplet to which relaxation is taking place), the importance of symmetry considerations is greatly reduced.¹²

We report here the results of a systematic study of multiphonon orbit-lattice relaxation of excited states in LaBr_3 , LaCl_3 , and LaF_3 , using a number of rare-earth ions as probes. Excited-state lifetime and quantum efficiency measurements in the optical and near-infrared regions were performed at 4.2°K to determine the spontaneous multiphonon transition rates, and at elevated temperatures

to ascertain that the nature of the processes were as described above. A detailed discussion of these experiments will be presented elsewhere.¹³

LaCl₃ and LaBr₃ are isostructural and have very similar static crystalline electric fields,¹⁴ with C_{3h} symmetry at the site of the rare-earth ion. The vibronic spectra of both have been studied,^{10,15} and there is a systematic correspondence of the phonon densities of states. The major features of the LaBr₃ vibronics are reflected in the LaCl₃ vibronics, scaled in energy as a consequence of the difference in the halogen masses. The phonon density of states cuts off at about 260 cm⁻¹ in LaCl₃, and at about 175 cm⁻¹ in LaBr₃. LaF₃ represents a completely different crystal system. The point symmetry at the rare-earth ion site is thought to be C_{2v} or lower,¹⁶ and the crystalline Stark splittings are typically two or three times larger than in LaBr₃ and LaCl₃. The vibronic spectrum has been observed,¹⁷ and indicates an energy cutoff in the optical phonon spectrum at 350 cm⁻¹.

A typical temperature dependence is shown in Fig. 1. Here the multiphonon decay of the E(⁶F_{3/2}) level of LaBr₃:Dy³⁺ is shown as a

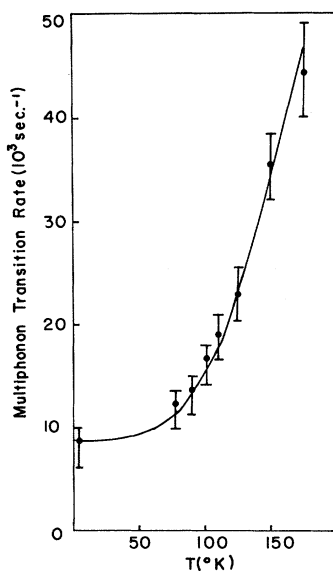


FIG. 1. The multiphonon transition rate from the E(⁶F_{3/2}) level of LaBr₃:Dy³⁺ is shown as a function of temperature. The theoretical fit shown represents the stimulated emission of five phonons of energy 155 cm⁻¹, whose sum is approximately equal to the transition energy gap of about 775 cm⁻¹. The error bars shown indicate absolute maximum probable error. The relative error between points is much smaller.

function of temperature. The data are fitted by a theoretical model involving the stimulated emission of phonons by thermally populated phonon modes. Here, in particular, we consider the emission of five phonons of energy 155 cm⁻¹, whose sum is equal to the transition energy of about 775 cm⁻¹. The temperature-dependent transition rate is then given by

$$W(T) = W_{\text{spont}} (\bar{n}_{155} + 1)^5 \\ = 8.8 \times 10^3 \left[\frac{\exp(155/kT)}{\exp(155/kT) - 1} \right]^5 \text{ sec}^{-1}.$$

These phonons are in the high-energy optical phonon region, and correspond to the lowest-order process consistent with energy conservation. Higher-order processes would have a far steeper temperature dependence than is observed. Although the model is admittedly crude, it provides strong evidence regarding the nature of these multiphonon emission processes. Analogous behavior has been observed in LaCl₃ and LaF₃, and is published elsewhere.^{6,7,13}

In Fig. 2 are plotted the spontaneous multiphonon transition rates for the three lattices as a function of energy gap. The exponential dependence of the rate on the gap is highly systematic and indicates the averaging out of the precise features of the interacting levels and phonon modes. The critical param-

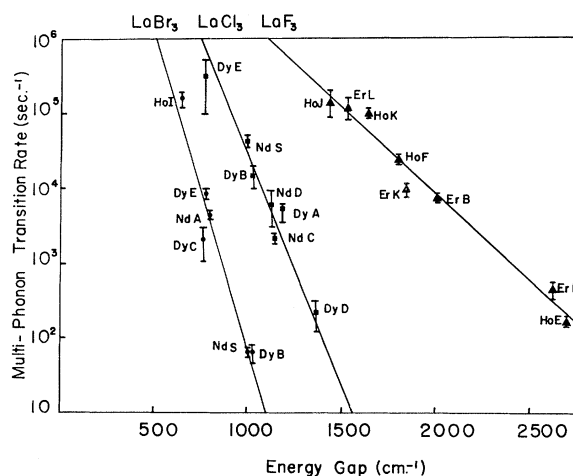


FIG. 2. The spontaneous multiphonon transition rates of a number of excited states of rare-earth ions in LaBr₃, LaCl₃, and LaF₃ are shown plotted against the transition energy gap. The designations of the states are according to Dieke (Ref. 1).

ter within a lattice is the energy gap, i.e., the order of the process, and therefore, in most cases, multiphonon transition rates are highly predictable on the basis of the behavior that is observed empirically.¹²

In Fig. 3 are shown the same data plotted against a normalized energy gap, where we have divided the transition energy by the maximum phonon energy, thus arriving at the effective "order" of the process. There are a number of striking features here. First of all, the LaBr_3 and LaCl_3 data fall precisely on top of one another. This is reasonable, in view of the fact that they have the same structure and nearly identical crystal fields. The only difference lies in the phonon density of states, which for LaBr_3 is a scaled-down version of that of LaCl_3 . When the energy gap is normalized to the phonon energy, this behavior is precisely what one might expect. In LaF_3 the rates have a somewhat different dependence on the effective order; we find the same rate as for LaBr_3 and LaCl_3 at an order involving one to three additional phonons. The density of phonon states for LaF_3 is quite different from that of LaBr_3 and LaCl_3 . Furthermore, the crystalline-field splittings in LaF_3 are typically two to three times greater than in the other two lattices, and it is not unreasonable to expect that the dynamic crystalline-field matrix elements (whose squares enter into the transition rate) will reflect the strength of the static parameters.¹⁸ The consequences of this situation would be that (1) the rates for LaF_3 for a given order would be faster than in the other two lattices; and (2) since the dynamic crystalline-field matrix elements should determine the convergence properties of the transition rates, the dependence on normalized transition energy should be a more slowly decreasing function in LaF_3 than in LaBr_3 and LaCl_3 . These are precisely the features that are observed in Fig. 3.

In conclusion, it has been shown that in LaBr_3 , LaCl_3 , and LaF_3 , the multiphonon orbit-lattice relaxation rates can be determined systematically by a single parameter, the transition energy gap. If the energy gap is normalized to account for the spread in the phonon density of states, the rates for LaBr_3 and LaCl_3 , which have nearly identical structures and crystal fields, have identical dependences on the effective order. In LaF_3 the systematics are maintained, and the faster rates and slow-

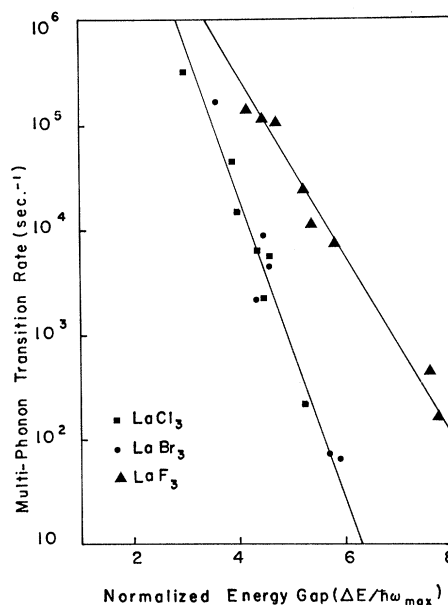


FIG. 3. The data of Fig. 2 are shown plotted against the normalized energy gap, where we have divided the transition energy by the maximum optical phonon energy for each lattice. In LaBr_3 the gap has been divided by 175 cm^{-1} , in LaCl_3 by 260 cm^{-1} , and in LaF_3 by 350 cm^{-1} .

er convergence with order can be readily explained through the qualitative difference in the phonon density of states and the much stronger crystalline field.

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VELOCITY OF OPEN-ORBIT ELECTRONS IN GALLIUM*

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A Doppler-shifted open-orbit resonance in gallium is described. From the separation of corresponding attenuation peaks for $\pm n$, the effective electron drift velocity along the propagation axis is determined.

The effect of open orbits on the attenuation of ultrasonic waves in pure metals was first discussed by Galkin, Kaner, and Korolyuk¹ in connection with the appearance of nonharmonic resonant-type oscillations in the transverse magnetoacoustic effect in tin. With acoustic propagation perpendicular to the magnetic field, $\vec{q} \perp \vec{H}$, energy is resonantly absorbed by electrons satisfying the condition for Doppler-shifted cyclotron resonance²

$$(1 + \langle v_x \rangle / v_s) \omega T = 2\pi n, \quad |n| = 1, 2, 3, \dots, \quad (1)$$

where v_s is the sound velocity, $\omega/2\pi$ the acoustic frequency, $\langle v_x \rangle$ the average electron drift velocity parallel to \vec{q} , and T is the period of the open orbit. The absorption peaks are determined by the repeat distance k_0 along the

orbit in reciprocal space with positions very nearly given by

$$H_n = \frac{qc\hbar k_0}{2\pi|n|e}, \quad \langle v_x \rangle / v_s \gg 1, \quad (2)$$

and characteristic linewidth by $\Delta H/H \sim (q\langle v_x \rangle \tau)^{-1}$, independent of n . Ultrasonic resonance periods of this type have appeared in cadmium,³ copper,⁴ thallium,⁵ and, most recently, in rhenium.⁶

When the sample is very pure and free of imperfections, however, the resonance lines may split at high acoustic frequencies. In this case, the unit factor in Eq. (1) cannot be neglected and the attenuation peaks occur at

$$H_{n\pm} = H_n (1 \pm v_s / \langle v_x \rangle) \quad (3)$$