not apply, but the fact remains that this expression describes the data better than any other simple expression we can find.

The data can also be fitted with the usual critical-phenomenon expression

$$\ln\epsilon = \ln a + b\,\delta h, \tag{2}$$

where a and b are constants. This type of analysis gives $a = 0.15$ and $b = 8.9$. The fit with Eq. (2) is not quite as good as Eq. (1) at small values of ϵ but it is certainly not to be ruled out.

There is no doubt that these samples show large deviations from the Saint James–de Gennes[2] or Ebneth-Tewordt[8] theories very close to T_C. In view of the great success of these theories at lower temperatures it seems most likely to us that the deviations are caused by critical phenomena[11] but, of course, this is not the only possible conclusion. The task now is to investigate the generality of the effect.

J. R. Clem, S. H. Liu, and C. A. Swenson have made important contributions to this work.

*Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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JAHN-TELLER EFFECT IN THE Γ EXCITON OF LiBr

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A previously unobserved splitting of the lowest exciton of LiBr is attributed to the exciton-phonon interaction in terms of a dynamical Jahn-Teller effect.

In this Letter we report on the optical properties of LiBr in the region of the lowest Γ-exciton peak, which appears as a doublet. Somewhat similar results have been obtained also for NaBr and NaI, but we confine the discussion to LiBr, because in the latter the splitting is better resolved. The data are shown in Fig. 1, which reports the imaginary part of the dielectric constant and the near-normal-incidence reflectivity at 55°K of a LiBr single crystal, cleaved in vacuum (about 5×10^{-7} Torr); the peak is clearly split into two components with a separation of 0.055 eV for ϵ_2 and 0.047 for R.

The features of the band structure which are relevant for the present experiment consist of a valence band associated essentially to the p states of the halogen ions, with a maximum at Γ_{15} split by spin-orbit interaction (Γ_6- and Γ_8-); the conduction-band minimum is at Γ_1 and the lowest exciton is associated to the $\Gamma_8- \rightarrow \Gamma_1$ edge. The experimental results in the literature are consistent with this picture,[1] but it appears that this purely electronic scheme is not sufficient to explain the structure shown in Fig. 1.

The spin-orbit splitting of the alkali bromides is about 0.5 eV and the binding energy is nearly the same[2]; these energies, confirmed also by two-photon absorption measurements,[3] are an order of magnitude higher than that of the observed splitting, and clearly rule out the attribution of the high-energy component of Fig. 1 to spin-orbit interaction, or to the envelope of the $n \geq 2$ members of the Wannier series. Furthermore, from the examination of the band structure calculations on the bromides,[4] on the basis of the magnitude involved and of the general trend of the energy bands, one can reject transitions either to other conduction-band minima, or from valence-band points other than Γ_8-. On the other hand, longitudinal-transverse splitting of the exciton, recently proposed,[5] seems hard to be supported in our case, since longitudinal ex-

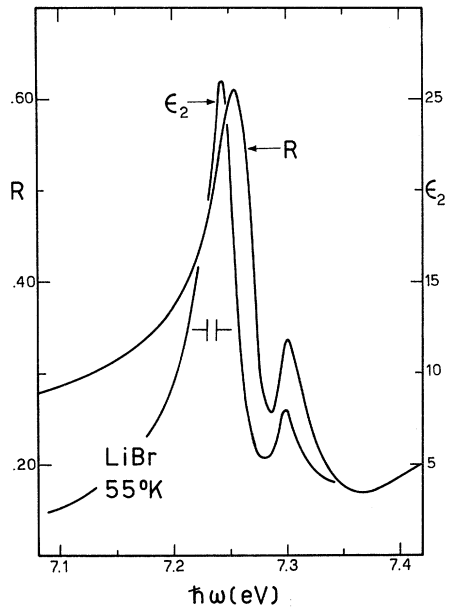

FIG. 1. Reflectivity and imaginary part of the dielectric constant of LiBr. ϵ_2 has been obtained by Kramers-Kronig analysis of the reflectivity measured up to 10.5 eV.

citons cannot be excited with light reflected at normal incidence on a single crystal. Moreover, measurements at 45° of incidence with *s* and *p* polarized light on LiBr have failed to yield meaningful differences. Also spatial dispersion, which seems to be causing a high-energy spike in the exciton of CdS,[6] can hardly be invoked for alkali halides, because of the strong localization and the large mass of their excitons.

So far, we have neglected the degeneracy of the exciton, arising from the degeneracy of the hole at Γ_{8-}. Among the causes which, after removing this degeneracy, could give a splitting, we should consider the exchange interaction between electron and hole, which, according to theoretical predictions,[7] introduces an additional state, not optically allowed, on the low-energy side. This, however, is in contrast with our observation on the additional peak: high-energy side and relatively high intensity. Finally also a splitting induced by a static stress field should be ruled out, because we have adopted a careful mounting of the sample in order to leave the surface relatively free of strains.

The above discussion has been confined to a purely electronic picture; in addition exciton-phonon interaction can give rise to different effects, besides the usual line broadening. The presence of noncubic vibrational modes distorts dynamically the lattice around the exciton; the hole is in a degenerate Γ_{8-} symmetry state, and therefore lattice modes like Γ_3 are effective in splitting it into two states, as has been shown for the case of the *F* center in Cs halides.[8] The spin-orbit interaction, relatively strong in the Cs halides, splits the excited state of the *F* center into degenerate Γ_{8-} and Γ_{6-} states, and the Γ_{8-} state is further split by the Jahn-Teller effect. The exciton problem, with respect to the symmetries involved, is very similar and can be treated on equal footing. Since the exciton consists of two particles endowed with a wave vector, the situation is more complex than that of a molecule or a localized excitation like the *F* center; however, because the exciton mass is large for alkali halides, a localized exciton model can be adopted. The energy involved in the observed splitting is found to be of the order of the phonon energy, thereby suggesting the presence of the Jahn-Teller effect. In particular, for LiBr the 0.055-eV splitting is close to the energy of the LO phonon[9]; this can be claimed also for the other alkali halides so far investigated, and it appears as a rather general feature of several fine-structure studies of exciton lines.[10-13]

Different approaches, also based on the exciton-phonon interaction, have been considered in order to justify the presence of additional structures in the exciton peaks. In particular coupled exciton-phonon states have been suggested in other ionic crystals.[10,11,13] The Jahn-Teller effect, on the other hand, has never been considered for this problem; yet, in the alkali halides, it must be present on very general grounds, because of the orbital degeneracy of the exciton states. The consequent breakdown of the Born-Oppenheimer approximation makes it necessary to consider the eigenstates of the full electron-phonon system. The two approaches probably do not contradict each other, but they are, perhaps, complementary views of the exciton-phonon interaction.

In conclusion, the data on LiBr indicate that the exciton-phonon interaction, which cannot be treated as a simple perturbation on the electron states, is responsible for the observed splitting. The problem certainly deserves further study, both theoretically and experimentally, in order to determine, among other things, the coupling constants for the Γ_3 and Γ_5 modes which are expected to be responsible for the observed effect. A more complete account of this research will be published soon.

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STIMULATED RAMAN SCATTERING BY POLARITONS

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Stimulated Raman scattering from polaritons has been observed in $LiNbO_3$. The measured splitting of 134 cm^{-1} between the 0° and 180° stimulated emission is in good agreement with infrared dispersion of the 628-cm^{-1} A_1 TO phonon. Threshold powers for the forward and backward stimulated emission are in fair agreement with the theory of polariton-stimulated Raman gain.

Coupling between the transverse optical (TO) lattice modes and the electromagnetic field in crystals leads to a strong dependence of the lattice mode frequency on wave vector.[1] The region of strong coupling, in which the lattice excitation (polariton) is of mixed phonon and photon character, has been widely observed in near-forward spontaneous Raman scattering[2-4] in crystals lacking inversion symmetry. We report in this Letter the observation of stimulated Raman scattering (SRS) from polaritons. Forward SRS at the polariton frequency has been generated in $LiNbO_3$, and, at slightly higher threshold power, backward SRS at the TO phonon frequency. Although SRS has been reported earlier[5] in other noncentrosymmetric crystals, the expected polariton character, as shown by the frequency splitting between the 0° and 180° stimulated emission, has not been previously observed.

Our $LiNbO_3$ crystal was cut to 4.4 cm length from an a-axis $[11\bar{2}0]$ boule[6] substantially free of multiple domains, with end faces polished approximately normal to the boule axis. The incident laser beam was polarized in the z direction and travelled in the xy plane at an angle from the boule axis of ~1°, sufficient to decouple surface reflections. The incident light was generated as 40-nsec pulses by an internally apertured 6943-Å ruby laser Q-switched by a Pockels cell, and focused near the crystal by a lens of 1-m focal length. The laser beam was in a single transverse mode with approximately Gaussian distribution; its spectrum consisted mainly of two or three sharp lines of width $\lesssim 0.05$ cm^{-1}, spaced by 0.35 cm^{-1}. At the crystal the beam diameter at half intensity was $(2.9 \pm 0.5) \times 10^{-2}$ cm.

Forward (polariton) SRS appeared at a threshold power of 0.95 ± 0.15 MW, corresponding to a power density at the beam center of $(1.0 \pm 0.2) \times 10^9$ W cm^{-2}. Threshold power was taken to be the laser power at which SRS conversion efficiency reached 0.02%. Backward (phonon) SRS was observed at threshold power of 1.3 ± 0.2 MW. At laser powers $\gtrsim 1.5$ MW, 0° and 180° scattering occurred together with 180° scattering having the higher efficiency. At a laser power of 1.7 MW the phonon SRS conversion efficiency was approximately 3% while the polariton efficiency was 0.1% reproducible to within a factor of 3. The SRS duration was ~20 nsec and coincided with the peak of the peak of the laser pulse.

Figure 1 shows typical SRS spectra. The 180° emission occurs near 631 cm^{-1}, which is in good agreement with the frequency of the A_1-symmetry TO mode of highest peak Raman cross section, as observed[7,8] in large-angle Raman scattering.