ZERO-PHONON TRANSITIONS OF COLOR CENTERS IN ALKALI HALIDES*

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In this Letter we consider certain features of the optical absorption spectra of point defects in solids which are analogous to those of the Mössbauer γ-ray spectra in solids,[1] and report the observation of the corresponding zero-phonon lines associated with some of the "F-aggregate" color-center bands in several alkali halides. Zero-phonon transitions, in which a photon is absorbed with no transfer of energy to the lattice phonons, appear as lines which, in the ideal crystal at absolute zero, should have a breadth determined only by the lifetime of the excited electronic state. Multiphonon processes give a band, sometimes with structure, which typically has a breadth of the order of the Debye frequency or greater.[2] In principle, there are both a broad (multiphonon) and a narrow (zero-phonon) component associated with any optical transition, the ratio of the intensities being determined by the strength of the coupling between the optical transition and the lattice modes.[1] If one can detect and identify the zero-phonon transition associated with any specific broad band, a great variety of experiments become feasible which are impracticable using only the broad band.

The integrated absorption of the spike associated with a particular broad band depends on the most probable number (S) of phonons involved in the transition, which can be estimated either from the zero-point breadth of the band (H) or, if the luminescence and absorption of the band correspond to transitions between the same pair of electronic levels, from the Stokes shift (Δ). If the frequency characterizing the modes dominant in broadening the transition is ω_D, then the integrated absorption of the spike relative to the band at absolute zero is

$$I_s/I_b = e^{-S} \approx \exp[-(H/2.5\hbar\omega_D)^2]$$

$$\approx \exp(-\Delta/2\hbar\omega_D). \qquad (1)$$

This criterion suggests the possibility of observing the zero-phonon transition in a number of electron-excess centers in the alkali halides. Such transitions have been observed for several defects in LiF [3-6] but were not interpreted in detail nor were similar spikes found in other alkali halides. Our investigation of "F-aggregate" cen-

ter absorption in several alkali halides has shown that these sharp lines observed in LiF are not peculiar to that crystal but are common to many of the alkali halides.

Most of the work has been carried out using a Cary 14R spectrophotometer with the sample held either at 4°K or at 15°K. Some of the half-widths were confirmed using higher resolution instruments, and a few runs have been made during warming of the sample to obtain a rough measurement of the temperature dependence of the spike intensities. All the samples have been blocks a few mm thick cleaved from Harshaw crystals, and the defects were produced by standard techniques of additive coloration and bleaching or by prolonged x or γ irradiation at room temperature.

The R_2 band has consistently shown a zero-phonon line in all of the crystals studied and usually shows additional structure probably due to transitions involving the emission of one or more phonons of a moderately well-defined frequency, as first suggested by Delbecq and Pringsheim.[3] These modes may be either localized modes or continuum modes at frequencies near the critical points of the phonon $\omega(k)$ surfaces where the density of modes per unit frequency becomes high. Figure 1 shows the R_2 band in several alkali hal-
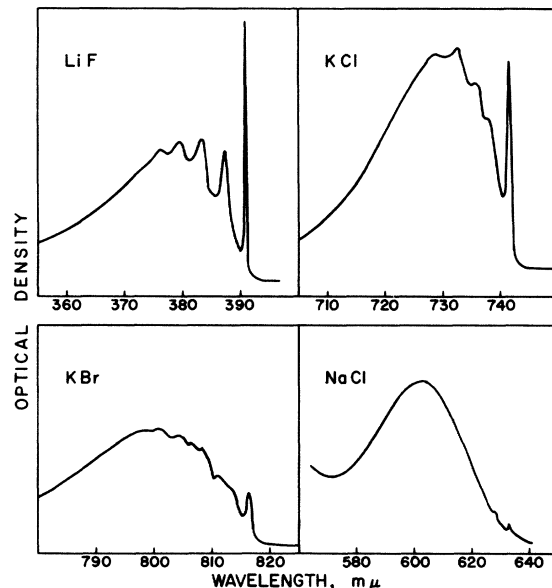

FIG. 1. The absorption spectrum of the R_2 band at liquid helium temperature in several alkali halides.

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Table I. Parameters for the R_2 absorption band and zero-phonon line in several alkali halides at liquid helium temperatures.

Crystal	Band peak λ_m (Å)	Bandwidth H (eV)	Zero-phonon line λ_0 (Å)	Linewidth (eV)	Relative Integrated Absorption I_s/I_b	Estimated S values $\ln(I_b/I_s)$	$(E_m - E_0)/\hbar\omega$	$H/2.5\hbar\omega$
LiF	3785	0.23	3907	0.0024	2×10^{-2}	3.9	3.2	7.5
NaF	4330	0.15	4475	0.0037	4×10^{-3}	5.5	3.7	5.0
NaCl	6025	0.12	6321	0.0015	7×10^{-4}	7.2	8.1	15
KCl	7310	0.05	7417	0.0009	3×10^{-2}	3.5	3.5	2.5
KBr	8000	0.06	8163	0.0013	7×10^{-3}	5	4	8.5

ides, including LiF where the observed structure is in good agreement with previous work. Table I summarizes the results for the different systems studied. The last three columns list the S values estimated on the basis of Eq. (1) from the relative intensity, from the half-width of the broad band, and from the energy separation between the zero-phonon spike and the peak of the band in units of the spacing between multiple-phonon peaks. The observed Stokes shift in R luminescence would imply S values far too large. This inconsistency, coupled with the fact that none of the narrow line series seen by others in LiF emission corresponds to a mirror emission band,[5,6] suggests that the excited electronic level in emission differs from that in absorption for this band.

Figure 2(a) shows the temperature dependence of the R_2 spike intensity in LiF, KCl, and KBr. In the Debye approximation, the theory of the Mössbauer effect[7] predicts that

$$\frac{I_S}{I_b} = \exp\left\{-S\left[1 + 4\left(\frac{T}{\theta_D}\right)^2 \int_0^{\theta_D/T} \frac{x\,dx}{e^x - 1}\right]\right\}$$

$$\approx \exp\left\{-S\left[1 + 6.6\left(\frac{T}{\theta_D}\right)^2\right]\right\}, \quad \text{for } T \ll \theta_D. \quad (2)$$

The θ_D's derived from the slope of the lines in Fig. 2(a) are in reasonable agreement with the energy spacing of the multiphonon peaks of Fig. 1. The appropriate temperatures are not the usual Debye temperatures, but instead appear to be close to those corresponding to the cutoff frequencies for the transverse acoustic modes in each crystal.[8]

At the lowest temperatures the widths of the lines [Fig. 2(b)] are essentially constant at a value much larger than the probable natural radiative

linewidth of the electronic transition indicating that this breadth apparently is not related to the interaction of the defect with the lattice vibrations. An experiment with isotopically pure Li^7F^{19} showed no significant narrowing, ruling out the possibility that this is isotope broadening. A previous observation[6] that the width of the R_2 spike in LiF
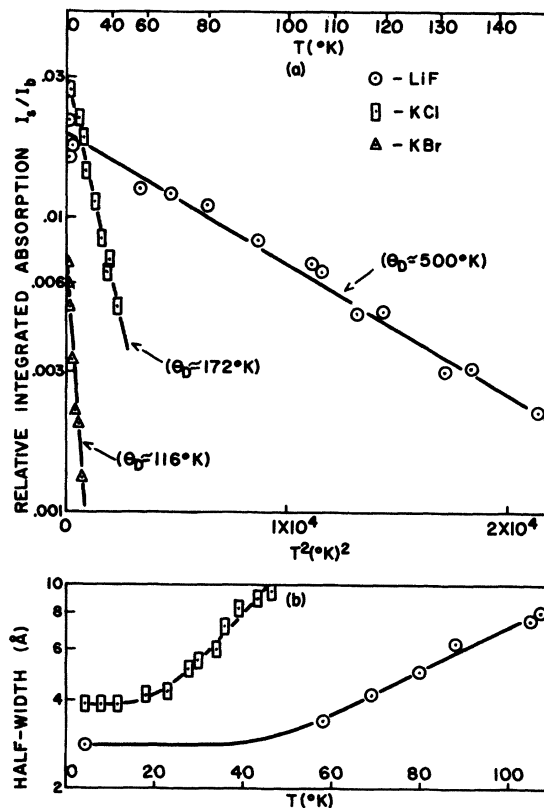

FIG. 2. The temperature dependence of (a) the relative integrated absorption, and (b) the half-width of the zero-phonon line on the R_2 band in LiF, KCl, and KBr.
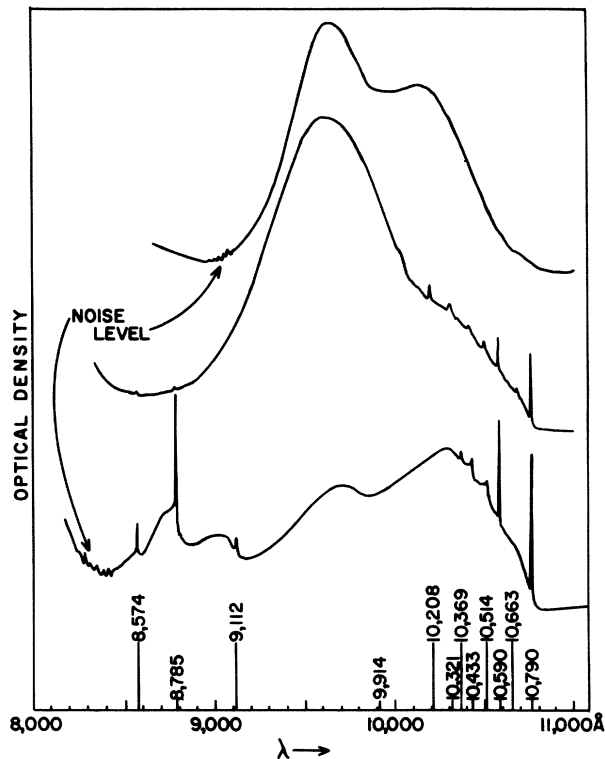
FIG. 3. Optical absorption in the region of the N bands for several samples of KCl at 4°K. Also are listed the wavelengths at which prominent sharp lines have been observed in these and other samples.

varies depending on whether the centers are formed by x-ray, electron, neutron, or α irradiation suggests that the broadening is due to residual strains or the interaction between defects, although we found no variation in width with sample treatment. A further possibility is the lifetime broadening resulting from the nonradiative decay to the initial state of the luminescent transition.

Figure 3 shows the optical absorption in the region of the N bands in several samples of KCl; similar complexity is observed in other alkali halides. Except in a few instances, namely the spikes at 8574, 8785, and 9112 Å, the presence

of a large number of overlapping broad bands prevents the identification of the broad bands to be associated with the various spikes. It is also clear that some of the bands in this region do not have observable spikes associated with them.

The two prominent spikes at 10 590 Å and 10 770 Å in KCl were observed to split into several components with the application of uniaxial stress in various crystalline directions. The symmetries and magnitude of the splittings were the same for both spikes. Study of the relative intensities of the components with polarized light determined that the optical dipole moments of the associated defects both lie in the [112] direction with a precision of $\pm 7°$.

In addition to the R_2 and various N spikes, several other spikes have been observed in the region of the M and R bands which are not obviously associated with any known bands. The M-band half-width indicates that $S \sim 8$ for the M center so that the zero-phonon line associated with the M band should be readily observable. Although spikes having about the expected wavelength and intensity have been observed, they do not show the dichroism or stress-induced splittings anticipated for the M center.

[1]The formal analogy between the theories for the two cases is discussed in E. D. Trifonov, Dokl. Akad. Nauk SSSR 147, 826 (1962) [translation in Soviet Phys. "Doklady" 7, 1105 (1963)] .

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