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V_3 Band in LiF[†]

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An optical absorption band is produced at 113 nm (11.0 eV) in both pure and Mg-doped LiF by irradiation with x rays at room temperature. This band, which appears to be intrinsic like the *F* band, is identified as the V_3 band. Its peak-wavelength position follows the same dependence on anion radius as has been found previously for alkali chlorides, bromides, and iodides.

Ionizing radiation produces in pure alkali halide crystals a defect center which absorbs light in the wavelength range where the unirradiated crystal is transparent – the *F* center. This center consists of an electron trapped at an anion vacancy. The irradiation must also produce a complementary trapped-hole center. When the irradiation is near room temperature, this is thought to be the V_3 center,[1] which absorbs light to the short-wavelength side of the *F* band, near the fundamental absorption edge of the perfect crystal. The V_3 absorption band has been studied in some detail in KCl,[2–7] KBr,[2–4] and RbCl.[4] The preponderance of this evidence suggests that the V_3 center is a molecular halogen center.[1,8]

The *F* center and some other electron and hole centers in LiF are well known, but the V_3 center has not yet been identified. Extrapolation of regularities found in other alkali halides[1] leads to the expectation that it should lie near 11 eV, just before the fundamental absorption edge. Previous investigations of the vacuum-uv region of irradiated LiF have indeed shown a peak at this location,[9,10] but it was not identified as the V_3 band. Our purpose is to discuss some new measurements and argue that this peak is, in fact, the V_3 band in LiF.

Optical-absorption measurements were made on both pure and doped LiF crystals in the range from 2 to 12 eV, using a Unicam SP-700 spectrophotometer and a McPherson vacuum-uv monochromator, model No. 235. Details of the operation of the latter instrument are reported elsewhere.[11] In the V_3-band region it was important to correct for stray light,[12] particularly in the doped crystals which had a large impurity absorption before irradiation. The pure LiF crystals were obtained from Harshaw Chemical Co. in 1968, and the impure ones in 1954. The latter contain of the order of 100 ppm Mg,[13] compared to about 1 ppm in the former.

To summarize some results which are described in more detail elsewhere,[11] irradiation of a pure LiF crystal at room temperature produces the *F* band at 250 nm and the band at 113 nm (11.0 eV) which we shall identify as the V_3 [see Fig. 1 (a)]. Irradiation of the Mg-doped crystal produces these same two bands, and, in addition, some electron

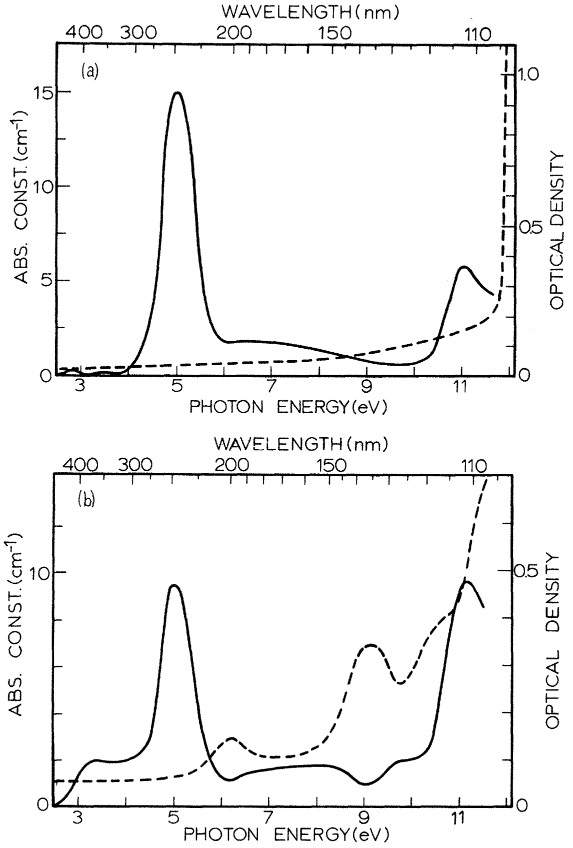

FIG. 1. Optical absorption of LiF crystals induced by x irradiation at room temperature (solid line). The absorption present before irradiation (dashed line) is subtracted from the post-irradiation curve to give the induced absorption. The absorption measurements were also made at room temperature (after Ref. 11): (a) pure LiF, containing about 1 ppm Mg; (b) impure LiF, containing 10–100 ppm Mg.

bands[14] at 380 and 310 nm [see Fig. 1(b)]. One notes that, in the pure crystal, the V_3 band is about one-half as high as the F band, whereas in the doped one the heights are nearly equal. Thermal decay of both bands occurs on annealing at 100° C or above.

Heavier irradiations of the pure crystal established that the V_3 band is intrinsic, like the F band, in that it shows no tendency to saturate (up to at least 10^{18} cm^{-3} or 15 ppm, assuming an oscillator strength of 1). The full width at half-maximum of the 113-nm band is $0.85+0.02$ eV. Bleaching the F band with 250-nm light at first leaves the V_3 band unaffected, as in KCl.[2,5] With prolonged bleaching, there is a small drop in the V_3-band height.

It was previously suggested that the 113-nm band is the LiF β band,[9,10] but a comparison of the pure and doped crystals shows that this identification cannot be correct. The β band is due to an exciton absorption which occurs next to an F center, and therefore its height is proportional to the F-band height. The 113-nm band, however, is not proportional to F-band height, being relatively much higher in a doped crystal than in a pure one (see, for example, Fig. 1).

A comparison with the other alkali halides shows that the 113-nm band is much more analogous to the V_3 band. Its broad width (broader than the F band's) is characteristic of the V_3 band, whereas the β band is typically much narrower than the F band. Furthermore the 113-nm band is well resolved from the fundamental absorption edge, like the V_3, while the β band is usually so close to the edge that it cannot be seen at all except at low temperature. Finally, the V_3-band area, relative to the F-band area, is considerably greater than the β-band area.

If the 113-nm band is the V_3, we may compare its peak-wavelength position in LiF and other alkali halides. Figure 2 shows the peak wavelength plotted against the anion radius (Pauling's values) on a log-log scale, for as many different salts as have been measured. (The absorption measurements were at room temperature for the LiF and at about 90° K for the other salts, but the temperature shift is only about 0.01 upward on the ordinate scale for this temperature increase.) Although the fluoride is widely separated from the other points, it follows the same dependence on anion radius as was previously described[1] for the other group of salts. To a first approximation, the position is independent of cation radius for this group of salts. The points are well approximated by the line drawn in Fig. 2 with slope

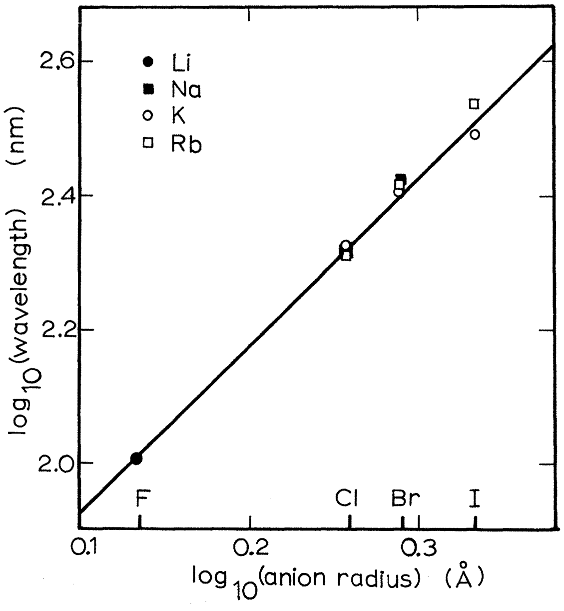

FIG. 2. Dependence of V_3-band peak-wavelength positions on anion radius. Li salt data from Ref. 11, Na from R. W. Christy (unpublished), and K and Rb from Ref. 1.

$\frac{5}{2}$, although we have no theoretical explanation for this slope.

Among the alkali halides, LiF is anomalous in some of its properties compared with the other salts, but its F-band position follows the same Mollwo-Ivey relation. We have identified the V_3 band in LiF, and shown that its position also is consistent with the other alkali halides.

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Study of Lattice Resonance Modes through Specific-Heat Measurements: KCl:Tl and KCl:Br†*

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The specific heat of KCl doped with 1-, 3-, and 5-mole% TlCl and of KCl-KBr mixed crystals has been measured between 1 and 30 °K. The frequency associated with the resonance mode, caused by the heavy impurity, was determined to be 51 ± 8 cm^{-1} (wave number) for KCl : Tl and 110 ± 10 cm^{-1} for KCl : Br, in close agreement with the resonance frequencies determined from thermal conductivity and infrared absorption. Our findings support the picture that the impurity modes in these cases are determined to a good approximation by the different mass of the impurity and not by a change in the local binding forces.

I. INTRODUCTION

The introduction of an impurity atom into an otherwise perfect crystal changes the vibrational spectrum of the pure crystal.[1,2] If, in particular, the impurity is heavy compared with the atoms of the host lattice, a new mode with a frequency within the normal phonon-frequency range appears. Much information about such resonance modes has been obtained from far-infrared spectroscopy[3] and thermal conductivity measurements.[4]

In this paper, we report a study of such resonance modes in KCl:Tl and KCl:Br through specific-heat measurements. As was first theoretically shown by Lehman and DeWames[5] and independently by Kagan and Iosilevskii,[6] a low-frequency resonance mode should substantially enhance the crystal-lattice specific heat at low temperatures. This prediction has later been confirmed experimentally in a few cases for doped metals.[7-9] In metals one has, however, the extra difficulty with the electronic contribution to the specific heat, which one has to subtract to get the true lattice specific heat, a procedure which adds to the uncertainty. The analyses of specific-heat data obtained on ionic crystals are more straightforward since contributions from mechanisms other than the lattice vibrations can usually be neglected.

The systems KCl:Tl and KCl:Br were chosen for several reasons. First, the ratio between impurity mass and host mass (the latter here taken as the mean of m_{K^+} and m_{Cl^-}) is reasonably high, 5.5 and 2.1, respectively. Second, the potassium and chlorine atoms have nearly the same masses and therefore the host lattice can be regarded as monatomic to a good approximation. This makes the comparison between experiment and existing theory especially easy. Third, both systems show a high