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Infrared Absorption by Impurity-Pair Resonant Modes in NaCl : F[†]

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New resonant-mode infrared absorption lines have been observed in NaCl with high concentrations of fluorine impurities. The quadratic concentration dependence of the strength of these lines indicates that they are due to pairs of fluorine impurities. At the resonant frequencies, the motion of some host ions appears to be as important as the motion of the impurities themselves.

INTRODUCTION

Many impurities in alkali halides induce an easily observed far-infrared absorption with concentrations of only 0.1 mole%. Essentially all this absorption can be attributed to isolated impurity ions at substitutional sites in the host lattice. However, a 1-mole% concentration of impurities should result in impurity-pair absorption comparable to the total absorption at 0.1 mole%. In general, this impurity-pair absorption would be difficult to observe above the isolated impurity absorption background. However, if the impurity pairs give rise to resonant or localized modes, ob-

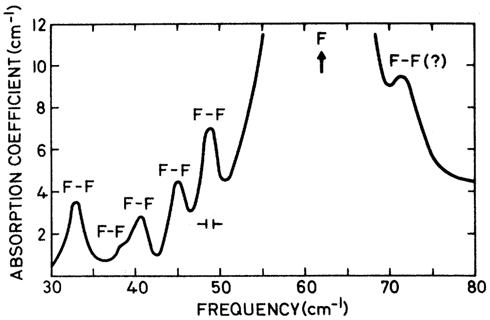

FIG. 1. Infrared absorption at 4.2 °K of NaCl with 1.8 mole% fluorine. Absorption by isolated fluorine impurities and by fluorine impurity pairs is denoted by F and F-F, respectively.

servation is somewhat simplified. Localized modes due to impurity pairs have been observed in a number of systems.[1] More recently, resonant pair modes have been reported in NaCl:Ag [2] and KCl:Na.[3] In this paper we report the observation of five, possibly six, low-frequency infrared absorption lines due to fluorine impurity pairs in NaCl.

EXPERIMENT AND RESULTS

The crystals were grown in air by the Czochralski technique. It was necessary to have up to 20 mole% fluorine in the melt in order to obtain 2 mole% fluorine in the crystal. The concentration of fluorine in the crystal was determined absolutely using a specific ion electrode method in which aqueous solutions prepared from the infrared samples were compared with solution containing known concentrations of fluorine ions. The relative impurity concentration of the samples was further checked by measuring an infrared absorption band known to be caused by isolated fluorine impurities. The transmission of the crystals was measured in a helium-immersion cryostat using the RIIC Michelson interferometer FS 720.

The absorption coefficient of NaCl with 1.8-mole% fluorine is shown in Fig. 1. The absorption line near 60 cm^{-1}, which peaks off scale, is due to isolated fluorine impurities. For low concentrations, the position of this line has been determined to be 59.5 cm^{-1} and its width to be less than 2 cm^{-2}.[4] For samples with an impurity concentration greater than 1 mole%, six new lines appear. The frequency, integrated absorption, and width at half-maximum of these lines are given in Table I. Two of these lines have been observed by Macdonald and Klein[5] and properly assumed to be pair lines. Figure 2 shows that the strengths of four lines depend quadratically on impurity concentration. The strength of the weak line at 38 cm^{-1} is difficult to measure with precision. However, this line seems to exhibit a quadratic concentration dependence also. The line at 72 cm^{-1} is difficult to measure for several reasons: The background absorption is high, the line is broadened by the higher density of states at this frequency, and absorption by polyethylene reduces the signal-to-noise ratio of the instrument in this region.

TABLE I. Pair-mode resonant absorption in NaCl : F.

Frequency (cm^{-1})	Integrated absorption[a] (cm^{-2})	Width[b] (cm^{-1})
32.7 ±0.1	5.0 ±10%	1.6
38.0 ±0.2	0.5 ±50%	1.6
40.2 ±0.1	3.0 ±10%	1.6
44.7 ±0.1	4.6 ±10%	1.6
48.4 ±0.1	5.7 ±10%	1.6
72.0 ±0.2	5.7 ±50%	3.0

[a] Results for 1.8 mole% fluorine concentration.
[b] Uncorrected for instrumental resolution of 0.8 cm^{-1}.

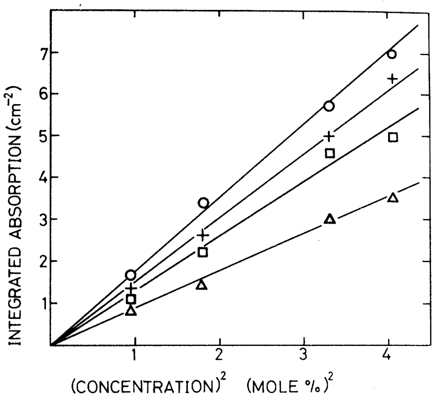

FIG. 2. Fluorine concentration dependence of the integrated absorption of four infrared resonance lines in NaCl : F. Data from the 32.7 cm^{-1} line are represented by +, from the 48.4 cm^{-1} line by ○, from the 44.7 cm^{-1} line by □, and from the 40.2 cm^{-1} line by △.

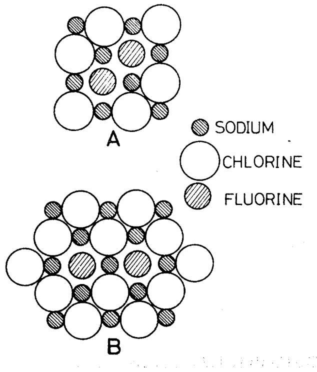

FIG. 3. Two fluorine-pair configurations in NaCl.

DISCUSSION AND CONCLUSIONS

One must conclude that at least five of the new lines are due to pairs of fluorine impurities. The next task is to assign a specific "molecular" vibration of a specific pair configuration to each line.

The sharpness of the lines suggests that a model based on the localized vibrations of a small number of atoms should give some useful information. Assuming the impurities are substitutional, there seem to be two important pair configurations, as shown in Fig. 3. It is difficult to see how more widely separated pairs could interact appreciably either directly or by means of a relaxation of the lattice. If we can decide how many atoms in each of these configurations participate in pseudolocalized vibrations, the number of infrared absorption lines can be predicted from group theory. If only the impurities themselves are assumed to vibrate appreciably, configuration *A* in Fig. 3 (D_{2h} symmetry) will contribute three lines and configuration *B* (D_{4h} symmetry) two lines. In fact, five and only five lines have been established as pair lines. However, one must remember that only very-low-frequency lines are observable. Resonant-mode absorption at frequencies appreciably higher than 60 cm^{-1} is not expected owing to the high density of states. Weak broad incipient resonances would be difficult to distinguish above the high background absorption of isolated impurities. It is implausible that all five infrared-active modes predicted by this simplest of models would occur at frequencies below the resonant frequency of the isolated impurity. In fact, after examination of Fig. 3, one easily becomes convinced that atoms other than the impurities will participate in pseudolocalized vibrations. For example, the sodium ion between the two fluorine ions in configuration *B* will be uncoupled to a large extent from the rest of the lattice for vibrations along the impurity-pair axis. This sodium atom would be expected, therefore, to participate in low-frequency resonant vibrations.

If the simplest model is extended to include the impurities and all their nearest neighbors, group theory predicts 27 infrared absorption lines. Clearly, this model is unnecessarily complicated. We can conclude that the impurities and a small number of their neighbors must be allowed to vibrate in order to obtain a qualitative description of our experimental results. A more accurate description will be difficult to achieve. Isotopic substitution would determine which atoms participate in which resonant modes. Unfortunately, there exist no other long-lived fluorine or sodium isotopes. In general, stress measurements can be useful in determining site symmetry, and such measurements are planned for the future.

In conclusion, we have observed five and possibly six low-frequency infrared absorption lines due to fluorine impurity pairs in NaCl. Although we cannot assign a pair configuration and vibration to each line, it is possible to conclude that the motion of some host ions is important.

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