

Asian Resonance

Modes Due to Clusters of Impurities in Alkali Halide Crystals

Abstract

When impurities are doped in otherwise pure crystals in large concentrations, the probability of cluster formation of impurities becomes quite appreciable. Formation of pairs, triplet cluster and higher order clusters takes place. Mutual interaction between these impurities gives rise to localized modes. Such modes have been observed in various systems. In poly atomic impurities such modes have been observed as side bands of the internal vibrations.

Keywords: Pair Modes, Triplet Clusters, Dipole-Dipole Interaction.

Introduction

For impurities dissolved in small concentrations in crystals, mutual interaction effects among them are not prominent. But there comes a stage when pairing or clustering of impurities becomes important with increasing concentrations. Then the mutual interactions among the impurities cannot be neglected. The pairing or clustering gives rise to localized modes and they are reflected in infrared, Raman or EPR spectra. Intensities of such absorption bands are quadratically dependent on the concentration of impurities. In alkali halides, many impurity pairs have been studied and detected by various techniques which will be discussed later. In most the cases the pair were obtained by high level of doping of impurities and making use of statistical probability of pair formation. But de Souza et al. (1970) have obtained pairing of U-centres in KCl by controlled technique with low concentration of impurities and could produce isolated pairs.

Objective of the Study

During several experiments on a number of alkali halide-impurity systems, it has been observed that for higher concentrations interactions between impurity ions becomes important and modes due to pairs and higher clusters are observed. In case of polyatomic ions, the coupling of internal vibrations of different ions may have a profound influence on the absorption spectrum. This may lead to asymmetric broadening of the absorption band and may give rise to extra features. Therefore it is important to understand mutual interaction between the doped impurities. The present review work aims to understand the origin of such interactions with different techniques.

Review of Literature

There has been large number of theoretical formulations to understand these modes. They have been studied by molecular models (Jaswal 1965, 1972), Green's function techniques (Gupta and Mathur 1976, 1980, Kalyani and Haridasan 1976) and coupled harmonic model (de Souza and Luty 1973). In molecular model approach, impurity and their nearest-neighbours only are assumed to take part in the motion while the rest of the crystal lattice is assumed to be at rest. In Green's function techniques a complex knowledge of the eigen states and eigen vectors of the host lattice is required and the model in principle yields an exact solution of the problem. The molecular model should give good results for impurities whose motions are highly localized so that the assumption of neglecting the motion of rest of the lattice other than the impurities is valid. De Souza and Luty (1973) have proposed a model of two coupled harmonic oscillators for a pair of impurities. They (De Souza and Luty 1973) have applied this model to U-centre pairs in KCl with quite satisfactory results. The coupling between the two harmonic oscillators is provided by the electric dipole-electric dipole interactions between the two impurities due to induced dipole moments during their vibrations. If the motion of individual impurity is highly localized than the motion of the lattice relative to the impurity can be neglected and rest of the lattice can be



S. S. Khatri

Associate Professor,
Deptt. of Physics,
North-Eastern Hill University,
Shillong

considered to be rigid. The Hamiltonian for two coupled harmonic oscillators can be written as:

$$H = \frac{1}{2}(m_1 \dot{q}_1^2 + m_2 \dot{q}_2^2 + m_1 q_1^2 \omega_1^2 + m_2 q_2^2 \omega_2^2) + B q_1 q_2 \quad (1)$$

where m_1 is the mass of the first impurity, m_2 that of the second, q_1 is the displacement of the first impurity and q_2 that of the second. ω_1 and ω_2 are the localized frequencies. The last term is the interaction between the two localized harmonic oscillators which is responsible for giving rise to side bands to the localized vibration. B is the coupling constant. If the impurities during their vibrations have induced electric dipole moments μ_1 and μ_2 respectively then the last term can be written as:

$$B q_1 q_2 = \frac{\mu_1 \mu_2}{R_{12}^3} [\hat{\mu}_1 \cdot \hat{\mu}_2 - 3(\hat{\mu}_1 \cdot \hat{R}_{12})(\hat{\mu}_2 \cdot \hat{R}_{12})] \quad (2)$$

$\hat{\mu}_1$ and $\hat{\mu}_2$ are unit vectors along $\vec{\mu}_1$ and $\vec{\mu}_2$ respectively and \hat{R}_{12} is the unit vector along \vec{R}_{12} , which is distance between the two dipoles. This interaction predicts the correct shifts. The sign of this interaction decides the position of side bands. If the sign of the interaction is negative the side band will appear on the low frequency side if it is positive then the side band will appear on the high frequency side of the localized vibration. A pair due to two dipoles in crystals will show infrared absorption when the net dipole moment of the system is non zero. In crystal lattices the two dipoles can be in the same plane or in different planes. When the dipoles vibrate in the same plane two types of situations may arise: (1) the two dipoles can vibrate in the same directions; i.e. they are in phase, or (2) they may vibrate in the opposite directions; i.e., they are out of phase. In the first case pairs may show up in infrared absorption. But in the second case because the cancellation of the dipole moments they will not show infrared absorption. However, they may give rise to Raman scattering.

In treating dipole-dipole interactions for large distances ($R \gg a$, the lattice constant) the dipolar interaction would be screened by the polarization of the host lattice and the dielectric constant of the medium giving rise to a correction factor. But for alkali halides for small distances, the corrections from screening by dielectric constant and local field effects are very close to unity (de Souza and Luty 1973).

The first experimental evidence for pair modes was obtained from Raman scattering from Ag^+ pairs in NaCl by Moller et al. (1970). Ag^+ ions induced a peak at 47 cm^{-1} in NaCl which remained unexplained theoretically by earlier workers. The intensity of this band was found to be increase nearly quadratically with the Ag^+ concentration. Moller et al. (1970) have calculated the frequency of a vibrating Ag^+ pair occupying second nearest-neighbour site in the [110] directions, on this basis of the assumption that only the nearest-neighbour Cl^- ions contribute to the pair vibration. they obtained 47.5 cm^{-1} as the frequency of the pair mode which was in excellent agreement with the experimentally observed value. Templeton and Clayman (1971) have observed pair mode in $\text{KCl}:\text{Na}^+$ system whose intensity showed quadratic dependence on the Na^+ ion concentration. Jaswal (1972) used molecular model to explain the pair mode. It was shown that the defect produces a

very large softening of short range force constants around itself. De Jong et al. (1973) observed a series of closely-spaced absorption lines in the $\text{KI}:\text{Rb}^+$ system. The origin of these lines has been explained as arising due to the Rb^+ pairs in KI by Ward and Clayman (1974a). Using a molecular model, they have calculated the resonant mode frequencies of the Rb^+ pairs in KI. Later on, Ward and Clayman (1974a, 1974c) have observed pair modes due to Na^+ , Cl^- and Br^- impurities in KI. The intensities of these bands were found to vary quadratically with the concentration of impurities. The experiments of Becker and Martin (1972) on infrared absorption of the $\text{NaCl}:\text{F}^-$ system revealed six peaks. The quadratic concentration dependence of the strength of these lines indicated that they arise due to the pairs of fluorine impurities. They suggested two types of pairs the nearest-neighbour and the second nearest-neighbour pairs responsible for these modes. Haridasan et al. (1973) employed Green's function techniques to explain the pair modes observed by Becker and Martin (1972). This model could explain all the infrared resonant modes due to pairs of impurities, at least in a qualitative way. Ishigama et al. (1972) observed infrared absorption at 16.5 cm^{-1} due to K-F impurity pairs in NaCl containing large concentration of potassium and fluoride ions. This line was not present in samples with high concentration of only fluoride or only potassium ions. A careful analysis by them indicated that the strength of the absorption line was proportional to the product of the concentrations of the fluorine impurity and that of potassium impurity. The most extensively studied pair mode system is the U-centre pairs in alkali halides. This has been studied experimentally as well as theoretically by de Souza et al. (1970, 1973) and Robert and de Souza (1974). Several other workers have studied this system theoretically (Kalyani and Haridasan 1976, Gupta and Mathur 1976, 1980) by using Green's function technique. De Souza et al. (1970) achieved U-centre pairs in KCl by thermal reaction of mobile interstitial H_2 molecules with F-centre pairs (M-centres) The observed pairs modes due to U-centre pairs in KCl were satisfactorily explained by model of coupled harmonic oscillators where the coupling between the two oscillators is provided by electric dipole- electric dipole interactions (de Souza and Luty 1973). Later on, Robert and de Souza (1974) observed pairs modes due to U-centres in many alkali halides, viz., KBr, KI, NaCl and RbCl. They confirmed that the main coupling between the H^- or D^- harmonic oscillators in various hosts was provided by the dipole-dipole interactions. Some vibrational lines were identified due to $\langle 200 \rangle$, $\langle 211 \rangle$ and $\langle 220 \rangle$ neighboring $\text{H}^- \text{H}^-$, $\text{D}^- \text{D}^-$ or $\text{H}^- \text{D}^-$ pairs in the crystals.

Infrared spectra of the $\text{KI}:\text{NO}_2^-$ system has been studied previously by Narayanamurti et al. (1966) for relatively large concentration of the NO_2^- ion in KI. Khatri and Verma (1983 Phys. Lett. **95A** 191, 1985 J. Phys. C: Solid State Phys. **18** 5935) have also made a detailed study of this system for large concentration of the NO_2^- ion in KI. Several

sharp bands in the high resolution infrared spectrum of the anti-symmetric stretching vibration of the NO_2^- ion doped in KI single crystals containing $\sim 10^{19}$ ions cm^{-3} were observed at 1.7 K. These extra bands arise due to interaction between the transition dipole moments during the anti-symmetric stretching vibration of the nitrite ions forming clusters (pairs and triplet clusters). These studies confirms that these bands arise due to the mutual interaction between the nearby NO_2^- ions in KI and not due to free rotations or librations of the ions.

Conclusion

The present study gives general experimental and theoretical background in order to understand the different kind of motional states and localised modes of ions substituted in alkali halide crystals. Different theoretical models have been described and important experimental techniques to probe these motional states have been discussed. By and large, the infrared techniques have yielded much more information than any other techniques in this field. From this study, the importance of high resolution work is evident for proper understanding of the complicated structures near fundamental vibration of molecular ions in solids.

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