

MOTIONAL STATES OF NO_2^- AND OTHER IONS IN KI SINGLE CRYSTALS

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SYNOPSIS

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This thesis deals with the behaviour of polyatomic molecular impurities in alkali halide crystals, their localized and reorientational states and the interaction effects among impurities. The thermal, mechanical and many other properties of solids are strongly dependent on the orientational degree of freedom of its constituents and impurities. Therefore a systematic study of different orientational motions of ions in solids may lead to better understanding of the properties of solids containing molecular impurities.

A number of small ions or dipolar impurities dissolved as solid solution in alkali halide single crystals in small concentrations are known to occupy substitutional positions with discrete orientations in the lattice (Barker and Sievers 1975). The equilibrium orientations of dipoles are determined by the directions of potential energy minima within the lattice site they occupy. The dipolar impurities at low temperatures can reorient themselves among the equivalent potential wells due to

overlapping of wave functions of the oriented dipolar states leading to tunnel splitting of the orientational degeneracy. The tunnel splitting is extremely sensitive to the details of crystal field due to the host lattice. Another interesting problem is that of modes due to pairs and triplet clusters of impurities in alkali halide crystals. At relatively higher concentrations, formation of pairs and triplet cluster of impurities are favoured. The coupling between the impurities in a pair or triplet cluster gives rise to localized modes.

We have studied the tunneling modes, and modes due to pairs and triplet clusters of the NO_2^- ions doped in KI single crystals at 1.7 K. The nitrite ion is a bent dipolar ion. When it is doped in potassium iodide crystal it replaces the iodide ion such that its dipole moment points in the $[110]$ direction with its O-O axis along the $[001]$ direction in the KI lattice. It has a dipole moment of 0.97 Debye in KI (Sack and Moriarty 1965). This large dipole moment indicates that it is off-centred and is displaced along the $\langle 110 \rangle$ direction. Hence it has twelve equilibrium orientations. At very low concentrations of the impurity ($\sim 10^{17}$ ions cm^{-3}), the ν_3 vibration (antisymmetric stretch) of the NO_2^- ion shows multiplet structure. We have explained this structure as resulting from the tunneling

of the ion among the twelve $\langle 110 \rangle$ equivalent potential wells for the ion in the KI lattice (Khatri and Verma 1983a). The tunneling of the ion in KI has been explained in terms of the Gomez, Bowen and Krumhansl model (Gomez et al 1967). From these studies we have found that the probability for the tunneling of the ions among the next nearest-neighbour wells is largest whereas nearest-neighbour tunneling probability is small. From the observed splittings, we have estimated the potential barrier heights for different types of tunneling motions of the NO_2^- ion in KI. At relatively higher concentrations ($\sim 10^{19}$ ions cm^{-3}), the infrared spectra of the $\text{KI}:\text{NO}_2^-$ crystals at 1.7 K in the ν_3 fundamental vibration region of the NO_2^- ion shows many distinct side bands on both sides of the main ν_3 absorption peak. The intensities of these side bands show non-linear (roughly quadratic) dependence on concentration. The structure on the low frequency side is more pronounced than that on the high frequency side. These side bands have been explained as arising from the electrostatic coupling between the transition dipole moments of the NO_2^- ions occurring in pairs and triplet clusters. We have considered different types of pairs and triplet clusters of the ions in KI and their calculated mode frequencies are in reasonable agreement with the experimental observations (Khatri and Verma 1983b). The calculations are based on a

coupled harmonic oscillator model (De Souza and Luty 1973) where the coupling is provided by the interaction between the transition dipole moments of the NO_2^- ions during their ν_3 vibrations. From these studies we have estimated the magnitude of the transition dipole moment of the NO_2^- ion in KI.

Temperature dependent studies of the localized modes can provide useful information about the interaction between the local mode and lattice phonons. There have been numerous studies, both experimental and theoretical (Barker and Sievers 1975) on the temperature dependence of the width, position and intensity of local modes and resonant modes of several substitutional impurities in alkali halide hosts but hardly any study on infrared active gap mode has yet been possible. The reason is that the difference band absorption of the host lattice dominates the spectral region near the gap and thus masks the impurity induced absorption in the gap above around 10 K. It would be of considerable interest to study the temperature dependence of the gap modes in a suitable system and see whether similar mechanism can explain the temperature dependent effects for the gap mode which have been so successful in understanding the temperature dependent effects for the local and resonant modes.

The NO_3^- ion substituted in KI induces two gap modes at $\sim 73 \text{ cm}^{-1}$ and $\sim 88 \text{ cm}^{-1}$ (Metselaar and Van der Elsken 1968, Eijnthoven 1970) and they appear as side bands to the ν_3 fundamental vibration of the NO_3^- ion in KI. We have investigated the temperature dependence of the half-width and centre frequency of the ν_3 fundamental and its combination with the 73 cm^{-1} gap mode from 1.7 to 77 K. Information about the variation of half-width and centre frequency of the gap mode as a function of temperature is extracted from this study which can be satisfactorily explained in terms of anharmonic interactions of the gap mode with lattice phonons (Khatri and Verma 1982).

This thesis consists of seven chapters. Chapter I introduces the problem and outlines the controversies and confusing interpretations given by earlier workers about the motional states of the NO_2^- and NO_3^- ions doped in KI.

Chapter II presents the theoretical background to understand the different kind of motional states and localized modes of ions substituted in alkali halides. A brief review on the tunneling states, pair modes and temperature dependence of localized modes of various impurities in alkali halide hosts is also given in this chapter.

Chapter III deals with the experimental techniques like sample preparation, modified instrumental arrangement to attain higher resolution and helium cooled detector etc.

In chapter IV the tunneling motion of the NO_2^- ions in KI has been discussed. Studies made by earlier workers on the NO_2^- ion doped in alkali halides have been briefly described. From the observed splitting of the ν_3 fundamental vibration of the NO_2^- ion in KI, we have calculated various tunneling matrix elements. We have also calculated potential barrier heights for different types of tunneling motions of the NO_2^- ion in KI. From the magnitudes of these matrix elements and barrier heights, conclusions have been drawn about the nature of tunneling motions performed by the ion.

Chapter V contains the discussion of the modes arising due to pairs and triplet clusters of the NO_2^- ions in KI. In this chapter we have calculated the interaction energies between the permanent dipole moments of the NO_2^- ions and also between the induced dipole moments of the ions during their ν_3 vibration when the NO_2^- ions form pairs and triplet clusters in KI. From this we have calculated the position of various satellite bands observed in the vicinity of ν_3 vibration of the NO_2^- ion. We have also estimated the value of the induced (transition) dipole moment of the ion during its ν_3 vibration.

In chapter VI we have discussed the temperature dependence of the half-width and frequency shift of the 73 cm^{-1} gap mode of the NO_3^- ion in KI. From this study we have estimated the values of the effective Debye temperatures θ_C and θ_D , and coupling coefficients β , δ and $\alpha(A_{1g})$, which provide clues to the nature of coupling of the gap mode with lattice phonons.

The last chapter presents the conclusions derived from the present work.

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