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Tunnelling motion of dipolar impurities in alkali halides: The KI : NO_2^- system

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Abstract. Motional states of the NO_2^- ion doped in KI single crystals have been investigated using high-resolution infrared techniques. At very low concentrations of the impurity, the antisymmetric stretching vibration (ν_3) of the NO_2^- ion shows multiplet structure at 1.7 K. This structure can be understood in terms of contributions of different types of tunnelling motions of the NO_2^- ion among the twelve equivalent potential wells in the KI lattice. An attempt has been made to give an estimate of the potential barrier hindering reorientation of the ion in the KI lattice.

1. Introduction

Many dipolar impurities substituted in alkali halides in small concentrations are known to occupy discrete orientations in the lattice and perform different types of motions in multi-well potentials. The mixing of the oriented dipolar states may lead to the tunnelling of the ion among the equivalent potential wells in the crystalline lattice resulting in a multiplet of tunnelling levels. There have been a large number of experimental and theoretical studies of low-lying motional states of dipolar impurities substituted in alkali halides (Barker *et al* 1975).

The KI : NO_2^- system has been investigated previously by several workers using various techniques (Narayanamurti *et al* 1966, Evans and Fitchen 1970, Sack and Moriarty 1965, Rebane and Rebane 1973, 1974, Avarma and Rebane 1969) in an effort to understand the various types of impurity modes. Our interest in this system was aroused by an observation of the unusually large width of the ν_3 fundamental mode of NO_2^- in KI in high-resolution infrared spectra even at 1.7 K as compared with the sharp features for the NO_3^- ion in KI. Owing to the large observed dipole moment of 0.97 D for NO_2^- in KI (Sack and Moriarty 1965), it has been speculated that the centre of mass of the NO_2^- ion may not coincide with the centre of the I^- cavity and therefore may perform a tunnelling motion of the type observed for several monatomic impurities.

In this paper, we report our high-resolution infrared measurements on KI : NO_2^- for low-impurity concentrations at very low temperatures. At low concentrations ($\sim 10^{17}$ ion cm^{-3}). A very complex and temperature-dependent structure (at least six components) with an antisymmetric stretching vibration ν_3 is observed, and is interpreted as arising from the tunnelling of the NO_2^- ion among the twelve ⟨110⟩ equivalent equilibrium orientations of the ion at 1.7 K. At higher concentrations ($\sim 10^{18}$ ion cm^{-3} and above), several temperature-independent components showing roughly quadratic inten-

sity dependence on concentration have been observed. They presumably arise due to pair modes involving coupling among induced dipoles during ν_3 vibration of NO_2^- ions and will be reported on elsewhere (Khatri and Verma 1983). From the observed unequal spacings of the tunnel-split levels, we have attempted to calculate potential barriers for different types of tunnellings.

2. Experimental procedure and results

Single crystals of potassium iodide doped with potassium nitrite were grown by pulling from the melt using the Kryopolous technique. The starting materials were high-purity reagent-grade substances. To prevent OH^- contamination, potassium iodide was baked at $\simeq$400 °C in a nitrogen atmosphere for a few days after repeated grindings. After being pulled from the melt the crystals were cooled slowly over about a week to room temperature to avoid any inhomogeneities. The resulting crystals always contained both nitrite and nitrate ions in comparable concentrations, but by growing under nitrogen atmosphere more than 95% nitrate can be converted into nitrite ions. The NO_3^- and NO_2^- concentrations in doped KI crystals were determined by a spectrophotometric method. Crystals containing $\sim 10^{17}$ ion cm^{-3}, and of up to 20 mm thickness, were used in our experiments.

High-resolution infrared absorption measurements were made on a Perkin–Elmer Ebert-14 spectrometer equipped with a helium-cooled copper-doped germanium bolometer as a detector. Infrared radiation after dispersion from the monochromater was chopped mechanically and focussed on the sample held in a helium immersion cryostat. The temperature dependence of the fine structure with the ν_3 mode between 1.7 and 4.2 K was investigated by pumping on the helium in the immersion cryostat. The position of spectral lines was calibrated with respect to the known water vapour lines.

The infrared spectra of the NO_2^- and NO_3^- ions in alkali halides in the fundamental vibration region have been reported by Narayanamurti *et al* (1966). The strongest bands are found in the region of the ν_3 fundamental vibration centred around 1253 cm^{-1} for KI : NO_2^- while much weaker bands are observed corresponding to the symmetric stretch-

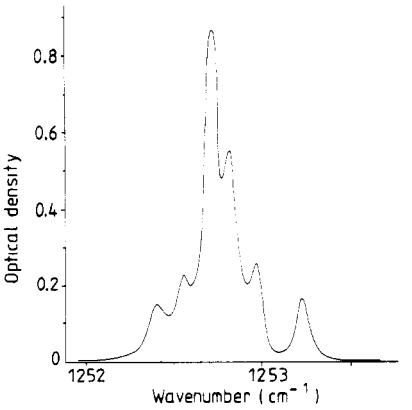

Figure 1. Infrared absorption spectrum of a 20 mm thick KI crystal containing $\sim 10^{17}$ NO_2^- ion cm^{-3} at 1.7 K in the ν_3 fundamental region; spectral resolution $\simeq$0.03 cm^{-1}.

ing ν_1 at nearly 1308 cm^{-1} and the bending mode ν_2 at 805 cm^{-1}. The ν_3 fundamental shows a half width of about 0.6 cm^{-1} without any apparent structure for crystals containing $\sim 10^{18}$ ion cm^{-3} at 1.7 K. When crystals of 20 mm thickness containing $\sim 10^{17}$ ion cm^{-3} are used, the ν_3 fundamental band at 1.7 K shows a splitting into six prominent components with an instrumental resolution of $\simeq 0.03$ cm^{-1}. The relative intensities of the components show a temperature dependence between 1.7 and 4.2 K. These measurements were repeated for several crystals specimens varying in impurity concentration after extensive annealing and all observations were in general agreement. A typical spectrum at 1.7 K is shown in figure 1. Above 4.2 K the widths of the lines become large and it becomes difficult to identify the individual components. At the low concentrations used, the intensity of the ν_1 fundamental band is too low to be measured accurately even with crystals several cm thick and therefore we confined our measurements to the ν_3 fundamental region.

3. Discussion

There are basically two approaches to understanding the low-lying motional states of defect ions in alkali halide crystals. The first was proposed by Devonshire (1936) and the second by Gomez *et al* (1967; hereafter referred to as the GBK model).

The first model assumes that the defect ion is a rigid rotator with angular coordinates (θ, φ) which is subjected to a potential $V(\theta, \varphi)$ having octahedral symmetry. The effect of the potential is to lift the $(2J + 1)$-fold degeneracy of the Jth rotational levels. The potential function used by Devonshire can account for impurities that have minima in the ⟨100⟩ and ⟨111⟩ directions. Later this model was extended by Beyeler (1972) by including higher-order spherical harmonics with minima in the ⟨110⟩ direction in the potential function. The NO_2^- ion in KI is displaced along the ⟨110⟩ direction with its dipolar axis along the same direction. The motion of the ion involves centre-of-mass motion together with angular displacements. The tunnelling among different equivalent wells is difficult to explain in terms of rotations about the three principal axes that pass through the centre of mass. It is therefore expected that the motion of the centre of mass of the ion in KI may be similar to that of an off-centre monatomic impurity in an alkali halide, such as Li^+ in KCl (Hetzler and Walton 1973) and Ag^+ in RbCl and RbBr (Kapphan and Luty 1972). Hence the tunnelling motion of the NO_2^- ion in KI can be better understood using the second model, the GBK model, which assumes that a point mass is subjected to a potential produced by the crystalline field of the host lattice, having minima at various points. In order to agree with the symmetry of the lattice surrounding the impurity, the well minima can be considered to be displaced along the six ⟨100⟩ directions, the eight ⟨111⟩ directions or the twelve ⟨110⟩ directions. In the absence of tunnelling, the eigenstates of the impurities would be six-, eight- or twelvefold degenerate as the case may be. Tunnelling removes the degeneracy, splitting the level into a number of components, and the actual states of the system will be linear combinations of the pocket states. These combinations can be found with the help of group theory.

The nitrite ion is a bent molecule of C_{2v} point group symmetry and the principal axes are as shown in figure 2. It is almost a prolate symmetric top with rotational constants $A = 4.22$ cm^{-1}, $B = 0.45$ cm^{-1} and $C = 0.43$ cm^{-1} about axes passing through the centre of mass of the ion (Narayanamurti *et al* 1966). When it is doped in KI, it substitutes an iodide ion. On the basis of the stress-induced dichroism in the infrared absorption of the

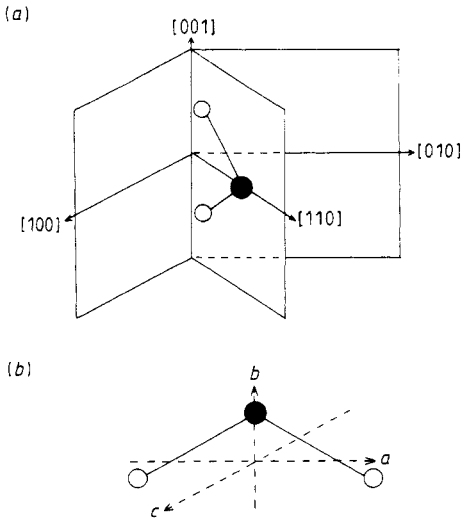

Figure 2. (*a*) Equilibrium orientation of the off-centre NO_2^- ion in KI at low temperatures, displaced towards the I^- ion nearest to the nitrogen atom. (*b*) The three principal axes of rotation *a*, *b* and *c* of the NO_2^- ion.

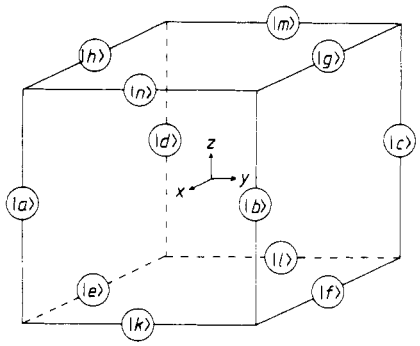

Figure 3. Minima positions and labelling of the localised harmonic oscillator basis (pocket states) for the XY_{12} model.

NO_2^- ion in KI, Narayanamurti *et al* (1966) found [110] orientation for the molecular axis (which is also the dipolar axis) and (110) as the molecular plane. Later on, Evans and Fitchen (1970) confirmed these findings with their stress-induced dichroism in the UV absorption of the NO_2^- ion in KI with the O–O axis along the ⟨001⟩ direction (figure 2). The dielectric relaxation measurements by Sack and Moriarty (1965) indicated a

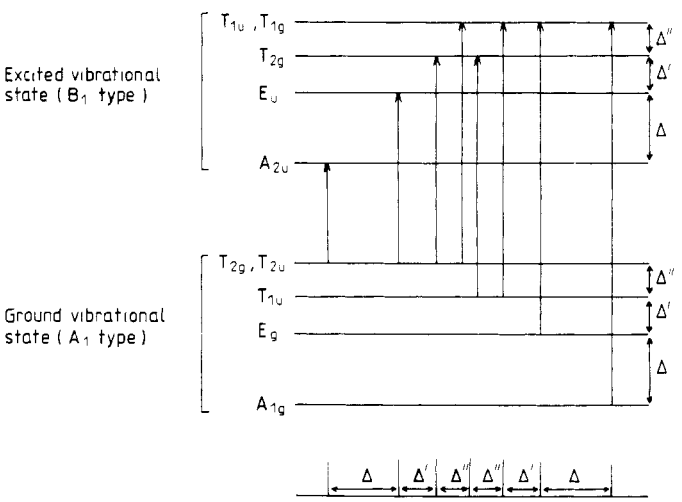

Figure 4. Tunnelling levels of the vibrational ground and excited states for the [110]-oriented dipoles (assuming the same structure in the ground and excited vibrational levels). The arrows indicate allowed optical transitions; the resulting absorption lines are given in the lower part of the figure. Here $\Delta = 6(\eta + \nu) = 0.27\ \text{cm}^{-1}$, $\Delta' = (2\mu + 2\sigma - 4\eta) = 0.15\ \text{cm}^{-1}$ and $\Delta'' = 4(\eta - \nu) = 0.13\ \text{cm}^{-1}$.

dipole moment of 0.97 D implying that the NO_2^- ion takes an off-centre position, displaced along the ⟨110⟩ direction in the I^- cavity because of the high polarisability of the I^- ion which would tend to attract the positive nitrogen atom. Therefore, the dynamics of the NO_2^- ion in KI should be similar to that of an off-centre ion with twelve potential well minima (figure 3) for the orientation of its dipole moment.

Measurements were made on the ν_3 fundamental of the ⟨110⟩-oriented dipolar ion NO_2^- in KI. Starting from the sharp ground state and excited state of the localised vibration, tunnelling among different equivalent wells leads to the splitting of the twelvefold orientational degeneracy of both these levels producing $E(A_{1g})$, $E(E_g)$, $E(T_{1u})$, $E(T_{2u})$ and $E(T_{2g})$ ground vibrational levels and $E(A_{2u})$, $E(E_u)$, $E(T_{2g})$, $E(T_{1g})$ and $E(T_{1u})$ excited vibrational levels (since the excited vibrational state ν_3 of the NO_2^- ion is of B_1 symmetry in the C_{2v} point group, the symmetries of the excited vibrational states are different from those of the ground state. However, the expressions for eigen-

Table 1. Tunnel-split lines for the KI:NO_2^- system (in cm^{-1}) as observed experimentally and as calculated. The relative intensities of these lines, calculated on the basis of a Boltzmann distribution of population and degeneracy of various components of the ground-state level, are given in the last column (this gives only the qualitative features, as the actual intensities will depend on transition dipole moments). The lowest-energy transition at 1252.14 cm^{-1} has not been observed, presumably because of its weak intensity.

Observed line position	Calculated line position	Calculated relative intensity (arbitrary units)
—	1252.14	1.88
1252.41	1252.41	1.88
1252.57	1252.56	1.88
1252.75	1252.69	5.87
1252.83	1252.82	2.10
1252.97	1252.97	1.59
1253.24	1253.24	1.00

values remain the same). The energy levels do not have equal spacings, and transitions between these levels give rise to the multiplet structure in the ν_3 fundamental region. The energy level scheme and electric-dipole-allowed transitions are shown in the figure 4. Observed and calculated line positions are given in table 1.

The wavefunctions and eigenvalues for the XY_{12} model have been worked out by Gomez *et al* (1967) by combining twelve pocket states group theoretically (figure 3). The energies of various levels obtained by them are given as

$$E(A_{1g}) = (E_0 + 4\eta + 2\mu + 4\nu + \sigma)/(1 + 4S + 2S' + 4S'' + S''')$$

$$E(E_g) = (E_0 - 2\eta + 2\mu - 2\nu + \sigma)/(1 - 2S + 2S' - 2S'' + S''')$$

$$E(T_{1u}) = (E_0 + 2\eta - 2\nu - \sigma)/(1 + 2S - 2S'' - S''')$$

$$E(T_{2g}) = (E_0 - 2\mu + \sigma)/(1 - 2S' + S''')$$

$$E(T_{2u}) = (E_0 - 2\eta + 2\nu - \sigma)/(1 - 2S + 2S'' - S''')$$

where

$$S = \langle a|n\rangle = \langle a|k\rangle = \ldots$$

$$S' = \langle a|b\rangle = \langle a|d\rangle = \ldots$$

$$S'' = \langle a|g\rangle = \langle a|f\rangle = \ldots$$

$$S''' = \langle a|c\rangle = \langle b|d\rangle = \ldots$$

are the overlap integrals. In order for the tunnelling model to be valid, the overlaps must be small enough to be neglected. The $|a\rangle, |b\rangle, |c\rangle, |d\rangle \ldots$ etc are pocket states.

$$\eta = \langle a|H|n\rangle = \langle a|H|k\rangle = \ldots$$

$$\mu = \langle a|H|b\rangle = \langle a|H|d\rangle = \ldots$$

$$\nu = \langle a|H|g\rangle = \langle a|H|f\rangle = \ldots$$

$$\sigma = \langle a|H|c\rangle = \langle b|H|d\rangle = \ldots$$

are the matrix elements, which are negative quantities, H is the impurity Hamiltonian and $E_0 = \langle a|H|a\rangle = \langle b|H|b\rangle = \langle c|H|c\rangle = \ldots$. The matrix elements η, μ, ν and σ are related to 60° (nearest-neighbour), 90° (next-nearest-neighbour), 120° (third-nearest-neighbour) and 180° (fourth-nearest-neighbour) tunnellings, respectively, of the NO_2^- dipoles. From the observed splitting, which is not equally spaced, it can be inferred that matrix elements other than η (60° tunnelling) are also important and our experimental results confirm this. Assuming the overlap integrals to be negligible, we may solve the energy level expressions for the matrix elements η, μ, ν and σ to give the best fit with the observed spacings. The best agreement is obtained when $E(T_{2g})$ is equal to $E(T_{2u})$. The values obtained for various matrix elements are as follows

$$\mu = 0.093\ \text{cm}^{-1} \qquad \sigma = 0.060\ \text{cm}^{-1}$$

$$\eta = 0.039\ \text{cm}^{-1} \qquad \nu = 0.006\ \text{cm}^{-1}.$$

These results suggest that the tunnelling of the NO_2^- dipoles among next-nearest neighbours (90° tunnelling) is the primary mode of tunnelling and 180° tunnelling also contributes significantly, whereas the 60° tunnelling is probably less important and 120° tunnelling contributes the least to the observed energies. The observed and calculated values of transition energies of the tunnel-split levels of the NO_2^- ion in KI are given in table 1 and are in reasonable agreement.

An estimate of barrier heights for the four types of tunnellings can be made with the help of simple model of a double harmonic oscillator (Gomez *et al* 1967) in which tunnelling occurs between two wells. Matrix elements relating two states for such a model can be written as

$$\delta = \hbar\omega a_0 (m\omega/\pi\hbar)^{1/2} \exp(-m\omega a_0^2/\hbar) \ldots \tag{1}$$

$$V_{0\delta} = \tfrac{1}{2} m a_0^2 \omega^2. \tag{2}$$

Here m is the mass of the defect ion, a_0 is the distance of the minimum from the origin (which is at the centre of the barrier), ω is the frequency of the particle in a single well and $V_{0\delta}$ is the barrier height corresponding to the matrix element δ. Equation (1) can be solved for ω and then the barrier height can be calculated from expression (2) which is the potential energy of the particle at the origin. The value of a_0 is x_0 for η, $2^{1/2}x_0$ for μ, $3^{1/2}x_0$ for ν and $2x_0$ for σ, where $2x_0$ is the displacement of the centre of mass of the

NO_2^- ion from the cavity centre. The displacement can be calculated from the knowledge of the dipole moment. The NO_2^- ion in KI has an effective dipole moment of 0.97 D directed from the centre of mass of the ion to the centre of the cavity, whereas its intrinsic dipole moment is 0.21 D (Sack and Moriarty 1965) in the opposite direction. Therefore the net dipole moment due to its displacement is 1.18 D directed towards the cavity centre. The absence of the negatively charged I^- ion from the cavity is equilvalent to a positive charge with magnitude equal to that of the I^- ion. The effective ionic charge of the I^- ion in KI has been found to be $e^* = 0.71e$ (Mitra 1969). This charge forms a dipole with the negatively charged NO_2^- ion. These two charges must have a separation of $2x_0 = 0.346$ Å.

Using this value of $2x_0$ the barrier heights corresponding to η, μ, ν and σ are found to be

$$V_{0\eta} = 1027.74 \text{ cm}^{-1} \qquad V_{0\mu} = 322.33 \text{ cm}^{-1}$$

$$V_{0\nu} = 409.65 \text{ cm}^{-1} \qquad V_{0\sigma} = 146.90 \text{ cm}^{-1}.$$

It is obvious that, because of large value of $V_{0\eta}$, the corresponding matrix elements for nearest-neighbour tunnelling are small in agreement with our interpretation.

4. Conclusions

The present studies show that the experimental results for the tunnelling of the NO_2^- ion in the $KI:NO_2^-$ system can be accounted for on the basis of the GBK model, and from this study it is evident that the motional states of the NO_2^- ion in the KI lattice are quite complex as compared with those in other alkali halide hosts. In other alkali halide hosts such as KCl (Narayanamurti *et al* 1966), motional states of the NO_2^- ion can be understood in terms of rotations of the ion about the three principal axes (a, b, c) since the centre of mass of the NO_2^- ion coincides with the centre of the cavity. In the KI lattice, because of the displacement of the centre of mass of the ion, the picture appears to be more complicated; the tunnelling motion is not merely rotational in character but a combination of translation and rotation. Tunnelling motion associated with the matrix elements μ and σ can be understood in terms of rotations about the a and c axes respectively together with translational motion, but in the case of η and ν it is much more complex. Using the one-dimensional approximation for tunnelling, barrier heights for different types of tunnelling motions have been calculated. The barrier heights obtained here are large compared with those obtained for the NO_2^- ion in other alkali halides by Narayanamurti *et al* (1966) which is mainly due to the complex nature of tunnelling motion of the NO_2^- ion in KI. On the whole our interpretation can explain the experimental observations quite satisfactorily.

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