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# Orientation of $NCO^-$ in KBr derived from polarized Raman scattering

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The recently introduced "behavior-type" analysis [J. F. Zhou, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **29**, 5509 (1984)] of polarized Raman spectra of vibrational modes is a *unique* method to determine the orientation of *static* linear molecular impurities in cubic lattices. The $NCO^-$ defect in KBr is shown for the first time to possess $C_{3v}$ point-group symmetry.

A substantial amount of theoretical and experimental work has been performed on substitutional molecular defects in alkali halides, such as $CN^-$ and $OH^-$, which exhibit, apart from the internal degrees of freedom, also librational and rotational modes. The orientation of their molecular axes is restricted by the cubic crystal field to well-defined directions most commonly lying along $\langle 100\rangle$, $\langle 110\rangle$, or $\langle 111\rangle$. Especially the reorientational motion between these equivalent equilibrium orientations has been thoroughly studied. The Devonshire model[1] and the tunneling model[2,3] give in a complementary way a satisfying description of this motion in the cubic multiwell potential.

Adequate modeling of the impurity potential strongly depends on the knowledge of the equilibrium orientations. Consequently, the determination of the site symmetry is an obvious and important experimental aim. Depending on the static or reorientational character of the impurity, different techniques can be applied. For the reorientational systems a molecular alignment by applied uniaxial stress or electric fields can be exploited, inducing a splitting of the energy levels of the elastic or electric-dipole system, which can be probed by, e.g., microwave absorption. Induced nonrandom distribution of dipoles is also detected in particular physical quantities, e.g., electrodichroism, electrobirefringence (Kerr effect), etc.

Polarized Raman measurements, performed on the tunneling sidebands of the stretching mode, yielded experimental evidence for the $C_{3v}$ point-group symmetry of $CN^-$ in KCl.[4] However, the small intensities and the poor resolvability of the tunneling sidebands put severe limitations on the general applicability of this approach.

The least accessible systems are unquestionably the static ones, for which no molecular alignment by an applied stress or electric field is possible. Except for the electron-spin-resonance technique, which is only appropriate for paramagnetic defects, the symmetry determination of these static defects is completely unexplored up until now.

We show that proper analysis of the polarized Raman spectra of the internal vibrational modes permits a simple and dependable symmetry determination of molecular defects in cubic lattices. For the stretching modes of *reorienting* diatomic molecular impurities in alkali halides, our method[5] yields a substantial experimental simplification, as no auxiliary external fields are required, and it turns out to be a unique approach for the *static* molecular impurities. In this communication the $C_{3v}$ symmetry of $NCO^-$ in KBr is revealed by a "behavior-type" (BT) analysis[6] of the polarized Raman spectra of both its stretching and bending modes.

A *polarized* Raman measurement involves the detection of the inelastic scattered light intensity as a function of the frequency shift with respect to the incident laser beam, in which the polarizations of both the incident and scattered light are considered as parameters. The polarized Raman intensity of a dynamical mode of a defect in a (cubic) crystal is given by the following expression:

$$I_{\alpha\beta}=kI_0\sum_n N_n(\bar{\alpha}^t T^{(n)}\bar{\beta})^2 \ , \tag{1}$$

in which $k$ is an instrumental efficiency factor, $I_0$ is the intensity of the exciting light beam, and $\bar{\alpha},\bar{\beta}$ are the polarization directions of the incident and detected scattered light. The equivalent orientations $n$ of the defect and their respective occupation numbers $N_n$ are explicitly taken into account. The form of the second-rank Raman tensor $T$ is dependent on the irreducible representation of the point group, to which the mode under study belongs. For each orientation $n$ the Raman tensor is transformed from the local defect reference frame, in which the group-theoretical form of the tensor is usually tabulated,[7] to the reference frame of the crystal axes.

The most important features of formula (1) are (i) the discrete average over all the equivalent orientations, and (ii) the fact that in cubic crystals the symmetry information, contained in the Raman tensor, is *not entirely* wiped out by this discrete average. The feature (ii) has been overlooked, until its potential usefulness was demonstrated in the BT method.[6] The BT method for *randomly* oriented defects is based on the experimental determination on accurately oriented samples of three independent intensity parameters (IP) $s$, $r$, and $q$, which are bilinear combinations of the Raman tensor elements:

$$s=8kNI_0(T_{12}^2+T_{13}^2+T_{23}^2) \ , \tag{2a}$$

$$r=8kNI_0(T_{11}T_{22}+T_{11}T_{33}+T_{22}T_{33}) \ , \tag{2b}$$

$$q=8kNI_0(T_{11}^2+T_{22}^2+T_{33}^2) \ , \tag{2c}$$

in which $N$ is proportional to the defect concentration. These IP, or equivalently the ratios $s/q$ and $r/q$, are derived from the polarized Raman intensities $I_{\alpha\beta}$, as obtained in the traditional perpendicular scattering geometry (Fig. 1). They can be expressed in terms of the $A_{1g}$, $E_g$, and $T_{2g}$ spectral contributions of the full cubic group $O_h$, according to which the polarized Raman data have up until now been classified.[5] The ratios $s/q$ and $r/q$ determine the observed BT and correspond to a set of possible point groups and representations for the mode under study, which are tabulated in Ref. 6.

To be specific, we concentrate on the stretching mode of a linear molecule. The free species belongs to the $C_{\infty v}$ point group and the $A_1$ stretching mode is characterized by a completely diagonal Raman tensor with two parameters, $\alpha_\perp$ and $\alpha_\parallel$ (the derived polarizabilities perpendicular to and parallel with the molecular axis, respectively), when expressed in the molecular reference frame with one axis along the molecular one. When this molecule is built into a cubic crystal, a unitary transformation has to be performed describing the orientation of the molecular axis along $\langle 100 \rangle$, $\langle 110 \rangle$, or $\langle 111 \rangle$ directions. The form of the *transformed* tensors is characteristic for the local symmetry and in the BT approach, this specificity is experimentally detectable in the $s/q$ and $r/q$ ratios. For a $C_{4v}$ symmetry the diagonal tensor tensor form is conserved and a zero $s/q$ ratio holds. The $C_{3v}:A_1$ and $C_{2v}:A_1$ tensors contain after transformation to the crystal reference frame also nonzero off-diagonal elements, yielding a nonzero $s/q$ ratio. A distinction between them can be made by considering the $r/q$ ratio which is 1 for the case of a threefold axis.

In the present paper, the BT method is applied to the $NCO^-$ in KBr, which was previously studied in several alkali halides by infrared absorption, partially because of the abundancy of lines in its vibrational spectrum (more than 80 fundamentals, overtones, and combination lines of both internal and external modes of the different isotopic species can be observed) and because of the presence of a Fermi resonance.[8-10] Very recently, infrared spectral hole burning was attempted in the vibrational bands of this defect.[11] The free $NCO^-$ is a linear molecule with three vibrational normal modes, i.e., a symmetric ($\nu_1$) and an antisymmetric ($\nu_3$) stretching mode, and a twofold-degenerate bending mode ($\nu_2$). In the KBr host lattice these internal modes are detected in the Raman spectra as local modes at 1207, 2173, and 630 $cm^{-1}$, respectively. The conservation of the twofold degeneracy of the bending mode, after the molecule is built into the crystal, is an argument to reject the $C_{2v}$ symmetry.[9] Sterical considerations favor the $C_{3v}$ symmetry, but up until now no experimental way was recognized to verify these speculations.

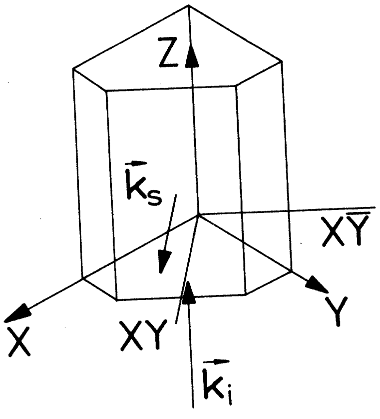

FIG. 1. Perpendicular scattering geometry used for polarized Raman measurements in a {110}-polished sample. The crystal axes are denoted *X*, *Y*, and *Z*. $\mathbf{k}_i$ and $\mathbf{k}_s$ represent the wave vectors of the incident and detected scattered light, respectively.

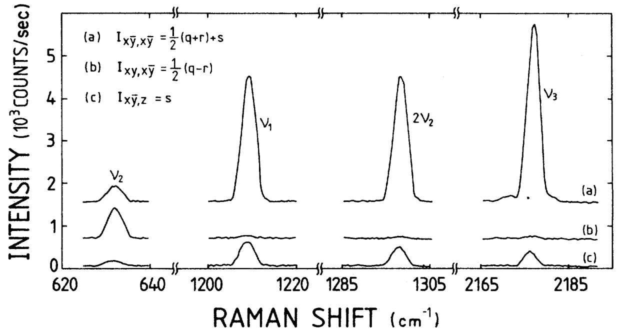

FIG. 2. Polarized Raman spectra of $NCO^-$ in KBr, representing (a) the $I_{x\bar{y},x\bar{y}}$, (b) the $I_{xy,x\bar{y}}$, and (c) the $I_{x\bar{y},z}$ intensities of the symmetric ($\nu_1$) and antisymmetric ($\nu_3$) stretching modes and of the bending mode ($\nu_2$) and its first overtone ($2\nu_2$). The subscripts on *I* denote the polarization directions of the incident and detected scattered light, respectively, with respect to the crystal axes. The spectra were recorded under 488-nm excitation ($Ar^+$, 500 mW) in a {110}-polished KBr sample containing 1 mol % KOCN, added to the melt. The statistical fluctuations are about 15 counts/s.

The polarized Raman spectra of KBr:$NCO^-$ are presented in Fig. 2. Both the symmetric and the antisymmetric stretching modes are found to possess a ratio $r/q$, which is within the experimental accuracy (5%) equal to 1. The $s/q$ ratios are different from zero. These IP ratios correspond to the $C_{3v}$ symmetry.

The bending mode at 630 $cm^{-1}$ can be handled in a similar way. The Raman measurements yield $s/q \neq 0$ and $r/q = -0.5$. This BT is specific for a $C_{3v}:E$ mode (No. 40 in Table VII of Ref. 6). The combined results for both the stretching and bending modes provide additional evidence for the $C_{3v}$ symmetry.

The polarized Raman spectra of the first overtone ($2\nu_2$) of the bending mode (1297 $cm^{-1}$), which yields the Fermi resonance together with the symmetric stretching mode, were also recorded. The values $s/q \neq 0$ and $r/q = 1$ correspond to the $C_{3v}:A_1$ mode. With the aid of group theory one can deduce that the first overtone of the twofold-degenerate bending mode of the $C_{\infty v}$ point group is a triply degenerate state, which splits into one nondegenerate $A_1$ and one doubly degenerate $E$ state.[12] Only the totally symmetric part ($A_1$) of this overtone is detected in the spectra.[9]

In this paper we have only focused on *linear* centers, which form the major part of the molecular impurities. It is not superfluous to mention that this method also applies to some extent to *nonlinear* impurities. For example, for the molecular ion $NO_2^-$, the free species of which possesses $C_{2v}$ symmetry, information about the orientation of the electric-dipole axis can be retrieved from the polarized Raman data. A Raman study of this molecular defect in several alkali halides is under way.

In conclusion, it is emphasized that the $\langle 111 \rangle$ orientation of the $NCO^-$ axis in KBr is retrieved from polarized Raman data *only*. The BT method leads to a reappraisal of polarized Raman scattering as a *competitive* technique for symmetry determination of molecular impurities. In view of our results, we feel that this detailed BT analysis, having its repercussions on all previous polarized Raman work in cubic crystals, should be routinely applied in the future.

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