POCKET VIBRATIONAL MODES DUE TO THE SILVER DEFECT IN POTASSIUM IODIDE#

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1. Introduction

At low temperatures, the silver impurity in potassium iodide is an on-center substitutional defect. This apparently simple defect system nevertheless produces a rich spectrum of defect-induced IR-active modes below the reststrahlen region of the host at low temperatures, which disappears as the temperature is raised to 25 K. The dominant absorption lines at 2 K are due to a resonant mode at 17.3 cm^{-1} and a gap mode at 86.2 cm^{-1}; several weaker features appear in the acoustic-phonon region. The on-center defect system becomes unstable at higher temperatures, with the Ag^+ ion moving away from the host-lattice site in a [100] direction by 25 K. As the temperature is raised, the low-temperature spectral features lose strength and a few new features appear, the strongest of which is a gap mode at 78.6 cm^{-1}. The temperature dependence of the on-center configuration as monitored in the far-IR is identical to that of the UV, Raman, and rf signatures of this defect system[1].

Although the abrupt temperature behavior suggests the existence of a strongly anharmonic potential, calculations based on a purely harmonic perturbed-breathing-shell model seem to describe correctly the low-temperature on-center configuration of the defect[2]. These calculations predict three nearly-degenerate gap modes of different symmetries with unusual displacement patterns: the displacements of the defect's fourth-nearest neighbors are more than an order of magnitude larger than those of the impurity or its nearest neighbors.

2. Model Calculations

Perhaps surprisingly in view of the unusual temperature behavior of KI:Ag^+, the zero-temperature on-center dynamics of this defect system are consistent with a perturbed harmonic shell model involving substantial force constant softening . In this model, each Ag^+ defect is characterized by its mass and by assumed defect–first-neighbor and relaxation-induced first-neighbor–fourth-neighbor longitudinal force constant changes which are obtained by fitting the observed IR-active T_{1u} resonant and gap mode frequencies at 17.3 and 86.2 cm^{-1}; all other force constants are assumed to be unperturbed. The model then predicts an E_g resonance at 20.5 cm^{-1}, in good agreement with the observed Raman peak at 16.1 cm^{-1}, as well as gap modes of A_{1g} and E_g symmetry with Raman strengths apparently too weak to be observed .

The three KI:Ag^+ gap modes predicted by the model have unusual properties. First, despite their different symmetries, the frequencies are very nearly degenerate. Second, the computed displacement patterns are strongly localized on the defect's fourth neighbor [e.g., (200)] potassium ions, away from the Ag^+ impurity and its nearest neighbors; hence the name "pocket modes." This is in sharp contrast to the usual localized or resonant mode behavior, including the KI:Ag^+ resonant mode at 17.3 cm^{-1}, where the displacement patterns are peaked at or adjacent to the defect, which is shared by the KI:Ag^+ resonant mode. The near-degeneracy of the predicted gap modes indicates that their frequencies are mainly determined by the local dynamics within each pocket, with the pockets being weakly coupled to produce the various symmetry modes.

3. Isotope Effect

Since the even-parity A_{1g} and E_g pocket modes were not observed in Raman scattering measurements[1], in agreement with the vanishing strengths predicted by the model calculations, another method of confirming their existence is required. One such approach is provided by the natural occurrence of a 7% isotopic abundance of $^{41}K^+$ in the host KI crystal. The presence of these isotopes on the Ag^+ defect's fourth-nearest neighbors can be expected to strongly mix the three nearly-degenerate pocket modes of various symmetry types. Based on nearly-degenerate perturbation theory, together with a calculation of the probabilities of the possible impurity/isotope configurations, the model predicts the appearance of a series of weak modes as a result of this isotope-induced mixing.

In order to confirm this prediction of the model, careful far-infrared measurements of the gap region of KI were performed. A weak "satellite" mode, on the low-frequency side of the unperturbed 86.2 cm^{-1} KI:Ag^+ gap mode, was observed[2]. The frequency and strength of this mode were found to be in reasonable agreement with those of the "isotope pocket mode" with the largest intensity and frequency shift predicted by the model.

In the course of these measurements, a more detailed study of the thermally-driven on- to off-center transition, as monitored by the strengths of the various far-IR modes, was performed. Because the displacement patterns of the resonant and gap modes are localized in such different spatial regions, their temperature dependences provide important clues to understanding the mechanism behind the thermal instability of the defect. In previously reported measurements[3], the temperature dependences of these two modes were found to be the same. Unfortunately, the uncertainties were much more pronounced for the gap mode, due to the presence of a temperature-dependent background produced by intrinsic difference-band absorption. In this study accurate measurements of the *derivative* far-IR absorption spectra were obtained. The resulting enhanced contrast for sharp spectral features allows the conclusion that the resonant mode and the pocket gap mode absorption strengths disappear with identical temperature dependences. Hence, the on- to off-center transition must involve not just the impurity moving in a static host lattice, but rather the simultaneous movement of the entire coupled defect/host system in the impurity region.

4. Uniaxial-Stress Measurements

Recent far-IR uniaxial-stress experiments reveal the unusual result that the pocket gap modes couple much more to the fully-symmetric (A_{1g}) strain than to the tetragonal (E_g) and trigonal (T_{2g}) strains[4]; other gap modes couple to A_{1g} and E_g strains with similar strengths. Calculations based on the perturbed-breathing-shell model phonons and a simple anharmonicity model suggest the presence of unusual pressure-induced microscopic displacements in the vicinity of the defect's fourth nearest neighbors. However, the sizes of the stress coupling coefficients of various symmetries imply that the anharmonic terms of the potential near the Ag^+ defect are comparable to those of other defects in KI. Thus, the on-center/off-center transition of KI:Ag^+ cannot be explained in terms of the anharmonicity of this defect system's potential. Finally, the A_{1g} and E_g coupling coefficients are both measured to be temperature dependent, with the E_g coefficient actually changing sign at 10 K; such behavior has not been found for other impurity-induced localized modes.

5. Conclusions

The low temperature dynamics of KI:Ag+ have been shown to be well-described by a nearly-unstable perturbed harmonic model which includes substantial force constant weakening. The most striking prediction of the model is the existence of three nearly degenerate pocket gap modes of different symmetries and with amplitudes strongly peaked on the impurity's fourth-nearest neighbors. The $^{41}K^+$ isotopes present on the impurity's fourth-nearest neighbors mix these nearly-degenerate gap modes, producing new pocket isotope modes with predicted frequencies and relative intensities in good agreement with the high-resolution far-IR measurements reported here, which directly confirm the existence of the nearly-degenerate modes and their unusual displacement patterns. The important result of the detailed analysis of the temperature dependence of the far-IR spectrum of this defect system is that both the low-frequency IR-active resonant mode and the IR-active pocket gap mode disappear at identical rates with temperature, in the range 0 K to 25 K, even though the dynamics of each involves different regions of the defect space. Thus, the present study has allowed for the first time an estimate of the spatial extent of the thermally-driven instability in this defect system: given the range of the pocket modes, established in this work, the entire coupled defect/host system must include at least 13 ions, including the impurity.

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6. References

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