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Phonon dispersion in the mixed crystal $K_{0.5}Rb_{0.5}I$

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The dispersion of optical-phonon branches has been measured in the mixed crystal $K_{0.5}Rb_{0.5}I$. A two-mode behavior is found for the transverse-optic branches, in the entire Brillouin zone, where two well-defined branches are observed around 10 and 12 meV. One longitudinal-optic mode has been observed close to the average frequencies calculated from KI and RbI. In addition there are some indications of a weak second longitudinal-optic mode within the frequency region of the transverse-optic branches. The results are compared with a breathing-shell-model calculation based on the pseudo-unit-cell approach.

In the past few years the lattice dynamics of mixed alkali-halide crystals has been extensively studied theoretically[1] but only to a minor extent experimentally. For $K_{1-x}Rb_xI$ there are infrared (ir) results from Fertel and Perry[2] and inelastic neutron scattering (INS) data from Aslam *et al.*[3] The latter measurements are limited to the investigation of the acoustical modes only and have been performed on a sample with a concentration $x = 0.5$ of the mixing ion. Since the disorder in the system is restricted to the sublattice which contains the lighter masses, typical phenomena caused by the disorder are expected to occur in the optical region. In fact, the acoustical branches do not show any anomalies and the measured frequencies are close to the average values between those of KI (Ref. 4) and RbI (Ref. 5). In the present work the INS investigations are extended to the region of optical vibrations for the same sample. The measurements were performed on the triple-axis spectrometers IN3 (HFR Grenoble) and TAS1 (FR2 Karlsruhe) within a 110 scattering plane of the crystal. A fcc unit cell was taken as a basis for the measurements although the translational symmetry is essentially disturbed. In contrast to the sublattice of the I^- atoms, which is assumed to be perfect, the sites of the cation atoms are statistically occupied either by K^+ or $Rb.^+$

Investigations of the elastic scattering revealed the existence of two different elastic structure factors corresponding to the odd and even reflections of the fcc lattice. In particular, no indications for an ordering of the cation sublattice were observed. The lattice constant turned out to be close to the mean value calculated from KI and RbI ($a = 7.17$ Å). Therefore, and from the occurrence of a single sharp maximum in the profiles of Bragg reflections, we conclude that the present crystal is rather homogeneous. The phonon measurement itself proved to be difficult. Due to the disorder the background scattering was increased and collective excitations in general appeared to be weak in the optical region. This disadvantage has essentially limited the accuracy of measured phonon frequencies. Typical counting rates with 40-ft collimation throughout were 10 to 20 min per point. In addition to the statistical errors the incoherent scattering might cause smaller shifts in the position of phonon peaks at energies where the phonon density of states is high. Some examples of the observed intensity distributions are shown in Fig. 1. We want to emphasize that different background levels in these scans result at most from different series of measurements on the two instruments and do not reflect a modulation in the diffuse scattering and a local ordering. Nevertheless the present measurements show that in the mixed system collective excitations are still defined within the whole Brillouin zone: The LO_1 mode, for instance, clearly shows a dispersion, and the different spectra obtained for geometries favorable either for longitudinal or transverse excitations prove a defined polarization of the modes (Fig. 1). The measured frequencies of the LO_1 mode are close to the mean values of KI and RbI. Although the TO branches are not fully resolved it is clear that there are two branches, TO_1 and TO_2. They are located within the frequency region of the TO branches of KI and RbI but are different from those modes.

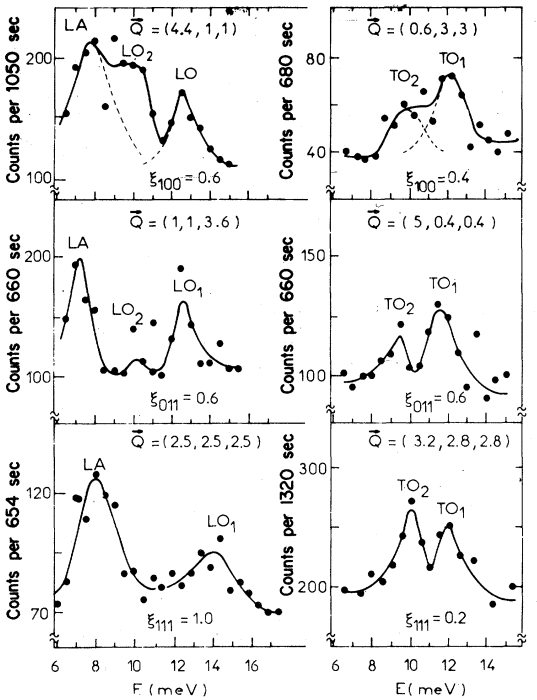

FIG. 1. Observed neutron scattering intensities for some particular wave vectors. Measurements performed at similar values of ξ but at different geometries show the polarization of the mode. There are some indications for a weak second LO_2 mode within the frequency region of the transverse modes.

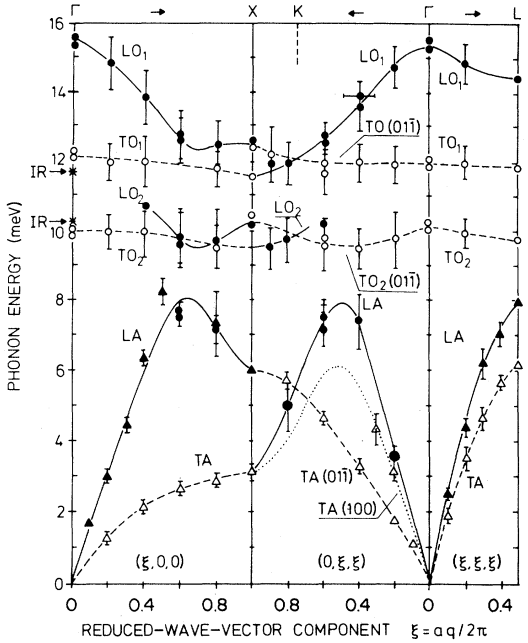

FIG. 2. Phonon dispersion in the mixed crystal $K_{0.5}Rb_{0.5}I$. Circles indicate the results of the present measurements and triangles indicate the data of Aslam *et al.* (Ref. 3). Solid symbols refer to longitudinal mode and open symbols to transverse mode. The ir results of Fertel and Perry are indicated by arrows. The heavy lines which connect the measuring points are drawn as guides to the eye.

There are some indications for a second longitudinal mode LO_2 but a corresponding branch could not be measured since the scattered intensity was too weak. The observed energy width of the phonon peaks is comparable with the instrumental resolution; therefore only an upper limit can be set by the present measurements. In Fig. 2, we show the overall results with an estimation of errors for the mode energies. These data are augmented by the acoustic phonon branches from Ref. 3.

According to the mass criterion from Chang and Mitra[6] a "two-mode" behavior is expected for $K_{0.5}Rb_{0.5}I$, which means that two modes should appear at frequencies close to those of KI and RbI. This behavior has already been shown to be true for the TO modes by the ir measurements[2] and its existence is now demonstrated for the entire Brillouin zone. A more difficult situation is found for the LO branches. In the mixed system one LO branch is clearly observed close to the average frequencies calculated from KI and RbI. In addition there are some indications for a weak second LO mode within the frequency region of the TO branches, but a complete dispersion branch could not be observed (see, in Fig. 1, the scan with $\xi_{111}=1$). This mode, if it exists, must be much weaker than the LO_1 branch.

Several models have been proposed to describe the lattice dynamics of mixed-crystal systems.[1] For the present crystal $K_{1-x}Rb_xI$ ($x=0.5$) the Rb ions can no longer be treated as single isolated impurities, and therefore the commonly used coherent potential approximation and the average t-matrix approximation may be less useful. We have used the breathing-shell model within the pseudounit-cell approach to calculate the dispersion relations of $K_{0.5}Rb_{0.5}I$. It assumes hard-core positive ions while negative ions consist of hard-core and deformable shells. The pseudounit cell for $K_{1-x}Rb_xI$ is assumed to have "hard" atoms constituting the "pseudomixing ion." Terms common to a breathing-shell calculation are utilized for the core displacement, the shell-core displacements, and the shell deformations. Details have been discussed in earlier articles[7,8] and will not be repeated here. Model parameters are deduced from physical observables of the pure end compounds. These are the elastic constants, long-wavelength transverse-optical-mode frequencies, high- and low-frequency dielectric constants, and the lattice constants. As a result, force constants are multiplied by molar weights that are related to the presence of the ion in the pseudounit cell; consequently, the dispersion relations will contain six "phonon" branches, which is exactly what we seem to observe taking into account a degeneracy of branches demanded by sym-

TABLE I. Short-range force constants and model parameters of $K_{0.5}Rb_{0.5}I$ (the symbols are those of Refs. 7 and 8).

A_{KI}	B_{KI}	A^1_{KI}	B^1_{KI}	k^2_{KI}	G^2_{KI}	Units
8.467	−3.006	1.282	0.051	154.023	737.87	$e^2/2v$
A_{RbI}	B_{RbI}	A^1_{RbI}	B^1_{RbI}	k^2_{RbI}	G_{RbI}	Units
9.156	2.407	6.507	−2.522	132.450	264.08	$e^2/2v$
Z_{KI}	Y_{KI}	Z_{RbI}	Y_{RbI}			Units
0.47	2.68	0.31	2.57			e

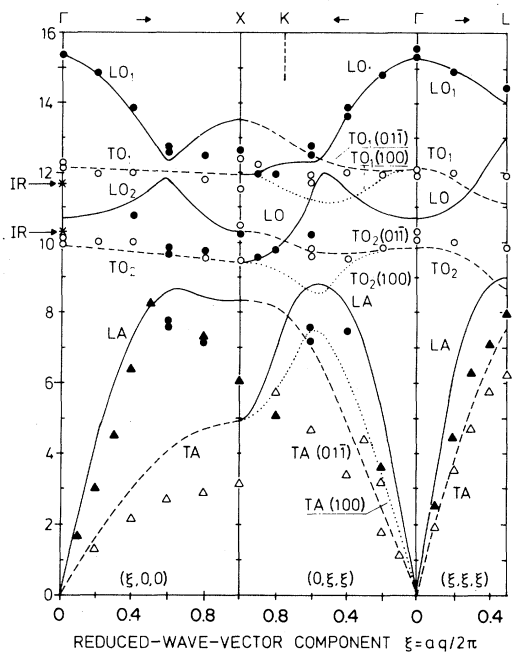

FIG. 3. Phonon branches calculated by the pseudo-unit-cell model. The model parameters are deduced from the elastic constants, the LO/TO Γ-point frequencies and the high- and low-frequency dielectric constants.

metry. Since the calculation starts with the knowledge of the macroscopic constants and the stability condition for each diatomic pair, the use of the Madelung constant is implied. Here, and as it was pointed out in Ref. 8, the parametrization of the stability conditions is considered through the phenomenological Madelung constants α_{KI}, α_{RbI}, which may also be thought of as order parameters of the mixed system. The calculated values show that the KI still behaves like a host lattice. While it is not difficult to find within the framework of the interaction considered in the model a value of α_{RbI} that approaches that of the alkali-halide lattice, our calculations show that this also implies unrealistic dispersion relations in directions other than [100].

The calculated dispersion relations were obtained considering first- and second-neighbor interactions, each of them weighted by an arbitrary concentration-dependent factor. These were chosen such that the calculated phonons at the Γ point agree within a few percent with those measured. Charge neutrality of the system was assured by the behavior of the acoustical modes.[8] Thus it was possible to establish the order of magnitude of the strength of ion interactions relative to the short- and long-range interactions of the pure compounds. The weighting factors imply a 70% strength for KI first-neighbors interactions, 70% for RbI first neighbors, about 100% for II second neighbors, and less than 1% for KRb second neighbors. Table I summarizes the force-constant numerical values. The calculated phonon branches are shown by the light lines in Fig. 3 together with the measuring points.

Since the present calculations do not represent a fit to the data the agreement is not satisfactory for all points, especially at the zone boundaries where, particularly for the acoustic modes, the calculated frequencies exceed systematically the experimental ones. Here a better description of the data might require an increase of the number of force constants by taking into account higher than second-order-neighbor interactions and/or a q dependence for the core-shell force constants. In spite of these difficulties the principal shape of the branches is well reproduced, which proves the pseudounit-cell model to be a valuable method when applied towards the understanding of crystalline mixed systems in which long-range interactions are not negligible.

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