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Two-mode behavior of mixed crystals

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A simple model has been developed to study the phonons in mixed crystals showing either one-mode or two-mode behavior. A nonrandomness parameter β is introduced to represent the phenomenon of two-mode behavior in mixed systems of the type $A_{1-x}B_xC$. When β is reduced to zero, the model gives one-mode behavior. Though the method developed is general in its application to any structure and any concentration x, the calculations have been done for $K_{0.5}Rb_{0.5}I$, a mixed alkali-halide system, the one which shows two-mode behavior in its class for all concentrations x in the range $0<x<1$. The theoretical results are in good agreement with the experimental ones.

INTRODUCTION

Studies of mixed systems have, in recent years, become a subject of considerable interest due to their wide applications in various fields of science and technology. Phonons, being one of the elementary excitations of solids, provide important and unique information about these materials. But the complexity of mathematical problems that arise in the study of lattice vibrations in disordered mixed systems has resulted in a variety of approaches and approximations.[1-14] Of all these attempts, the modified random-element-isodisplacement model of Chang and Mitra[5] is considered to be the most successful in predicting the behavior of mixed crystals. Even this formalism does not provide only two optical phonons at the zone center for pure crystals having two atoms per unit cell (it provides three) when reduced from the analysis of mixed crystals. Chang and Mitra have investigated that the appearance of local and gap modes is a necessary condition for the interpretation of two-mode behavior. This does not appear to find experimental support. In the present analysis, we have shown two-mode behavior with the local and gap modes occurring at $x\simeq 0$ and $x\simeq 1$, respectively, whereas at exact $x=0$ and $x=1$, we have only two optical-phonon frequencies.

Mixed alkali-halide crystals constitute an important class of systems. It has been observed that most of the mixed alkali-halide-crystal systems of the type $A_{1-x}B_xC$ occur in rock-salt structure, the same as that of their constituent members AC and BC, and show one-mode behavior in the entire composition range.[14,15] However, there has been found an exceptional case of $K_{1-x}Rb_xI$, which exhibits two-mode behavior[4,16] in contrast to other family members. The acoustical phonons in symmetry direction in $K_{0.5}Rb_{0.5}I$ were measured by Aslam *et al.*[14] using inelastic scattering of thermal neutrons. Recently Renker, Butt, and Massa[16] have reported their measurements of the dispersion of optical-phonon branches in the mixed crystal $K_{0.5}Rb_{0.5}I$ using inelastic neutron scattering technique. They have tried to explain the phonon dispersion data with a calculation on the breathing shell model based on a pseudo-unit-cell approach. But, as they conclude, their calculations do not represent a fit to the experimental data. It is for this reason that we have chosen $K_{0.5}Rb_{0.5}I$ as the subject matter of the present investigations. The present theory is applicable to any system showing either one-mode or two-mode behavior or both as the case may be.

THEORY

We use a modified rigid-ion model which has proved very good to explain the lattice dynamical properties of narrow-gap semiconducting mixed crystals.[17] The main features of the model are the following: (i) The effect of polarizability has been included by considering an effective charge parameter. (ii) The short-range forces are considered effective up to four neighbors. (iii) The eight force constants for the end members AC and BC are evaluated with use of the experimental values of the three elastic constants and the five phonon frequencies. (iv) The force constants for the mixed system $A_{1-x}B_xC$ are derived assuming a linear variation with x.

Starting with the above, we now develop the matrix to give phonon frequencies of the mixed system for its two-mode behavior as follows. We consider the mixed-crystal lattice constituted by two interpenetrating fcc sublattices numbered 1 and 2. The sublattice 1 is occupied by atoms of type C and sublattice 2 is occupied by atoms of types A and B. If the occupancy of sublattice 2 is randomly distributed in such a way that concentration of A is $(1-x)$ and that of B is (x), then the situation is of a homogeneous mixed crystal. In this case, the dynamical matrix will be given by, on similar lines to Eq. (8) of Kutty,

$$|[\omega^2 M_\alpha^\mu-\phi_{\alpha\alpha}^{\mu\mu}(q)]\delta_{\alpha\beta}\delta_{\mu\nu}-C_\alpha^\mu\phi_{\alpha\beta}^{\mu\nu}(q)|=0\ . \tag{1}$$

In a mixed crystal $A_{1-x}B_xC$, we have

$$C_1^C=1;\ C_2^A=(1-x);\ C_2^B=x\ ;$$

$$M_1^C=m_c;\ M_2^A=\frac{m_A}{1-x};\ M_2^B=\frac{m_B}{x}\ .$$

Also

$$\phi_{11}^{11}(q)=P,\ \phi_{22}^{22}(q)=(1-x)P,\ \phi_{22}^{33}(q)=xP\ ,$$

$$\phi_{12}^{12}(q)=Q,\ \phi_{12}^{13}(q)=Q,\ \phi_{22}^{23}(q)=P\ ,$$

where, P and Q are each 3×3 matrices given by

$$P=\begin{bmatrix}\begin{bmatrix}k&k\\x&x\end{bmatrix}&\begin{bmatrix}k&k\\x&y\end{bmatrix}&\begin{bmatrix}k&k\\x&z\end{bmatrix}\\\begin{bmatrix}k&k\\y&x\end{bmatrix}&\begin{bmatrix}k&k\\y&y\end{bmatrix}&\begin{bmatrix}k&k\\y&z\end{bmatrix}\\\begin{bmatrix}k&k\\z&x\end{bmatrix}&\begin{bmatrix}k&k\\z&y\end{bmatrix}&\begin{bmatrix}k&k\\z&z\end{bmatrix}\end{bmatrix},$$

$$Q=\begin{bmatrix}\begin{bmatrix}k&k'\\x&x\end{bmatrix}&\begin{bmatrix}k&k'\\x&y\end{bmatrix}&\begin{bmatrix}k&k'\\x&z\end{bmatrix}\\\begin{bmatrix}k&k'\\y&x\end{bmatrix}&\begin{bmatrix}k&k'\\y&y\end{bmatrix}&\begin{bmatrix}k&k'\\y&z\end{bmatrix}\\\begin{bmatrix}k&k'\\z&x\end{bmatrix}&\begin{bmatrix}k&k'\\z&y\end{bmatrix}&\begin{bmatrix}k&k'\\z&z\end{bmatrix}\end{bmatrix}.$$

The elements of matrices P and Q are given in our earlier paper for rock-salt structure.[17]

Substitution of these parameters in Eq. (1) gives

$$\begin{vmatrix}P-m_C\omega^2&(1-x)Q&xQ\\(1-x)Q^*&(1-x)^2P-m_A\omega^2&(1-x)xP\\xQ^*&x(1-x)P^*&x^2P-m_B\omega^2\end{vmatrix}=0\ , \tag{2}$$

where for pure crystal AC the dynamical matrix is, for $x=0$,

$$\begin{vmatrix}P-m_c\omega^2&Q\\Q^*&P-m_A\omega^2\end{vmatrix}=0 \tag{3}$$

and for pure crystal BC, for $x=1$,

$$\begin{vmatrix}P-m_c\omega^2&Q\\Q^*&P-m_B\omega^2\end{vmatrix}=0\ . \tag{4}$$

Since at $q=0$, $P=-Q$,[17] one of the solutions is $\omega^2=0$ for $U_A=U_B=U_C$ (i.e., the acoustic mode) for all values of x. If we analyze Eq. (2), we find that it exhibits, for all values of x, one-mode behavior. This, in general, is not necessarily the case. So, we have the occupancy of sublattice 2 as nonrandomly distributed in such a way that the $(1-x)$ A atom will interact with the $(1-x)$ A atom as well as the $(x\beta)$ B atom, where β is a nonrandomness parameter. Similarly, the (x) B atom will interact with the (x) B atom and the $(1-x)\beta$ A atom. Hence the dynamical matrix will now be given by

$$\begin{vmatrix}P-m_C\omega^2&(1-x)Q&xQ\\(1-x)Q^*&(1-x)(1-x+x\beta)P-m_A\omega^2&(1-x)x(1-\beta)P\\xQ^*&x(1-x)(1-\beta)P^*&x[x+(1-x)\beta]P-m_B\omega^2\end{vmatrix}=0\ . \tag{5}$$

If, however, the nonrandomness in the second sublattice of the mixed-crystal system is absent, we say $\beta=0$. This reduces the above matrix to give one-mode behavior.

It is very important to mention that, for pure crystals (i.e., the mixing components AC and BC), the above matrix can be reduced by putting $x=0$ or $x=1$, respectively, and gives only two optical frequencies at the zone center, i.e., no local modes or gap modes are obtained for the two exact cases of $x=0$ and $x=1$, in agreement with experimental facts. However, in the case of infinite dilution of the mixed crystal $A_{1-x}B_xC$, i.e., x becoming very small, we will get local and gap mode behavior.

The nonrandomness parameter β is evaluated for $K_{0.5}Rb_{0.5}I$, the case selected here for calculation, by fitting to the transverse optical phonon at zone center.[14]

RESULTS AND DISCUSSION

In view of the large core sizes and heavy masses of the constituent atoms of the mixed crystal $K_{0.5}Rb_{0.5}I$, the dispersion relations are obtained considering the short-range interactions up to four neighbors. The results are presented in Fig. 1. A comparison with experimental data provides good agreement. One interesting feature of the experimental observation[14] of the large width of the transverse optical phonon at the zone center is interpreted in our theoretical calculations by the presence of two optical phonons of nearly equal frequencies.

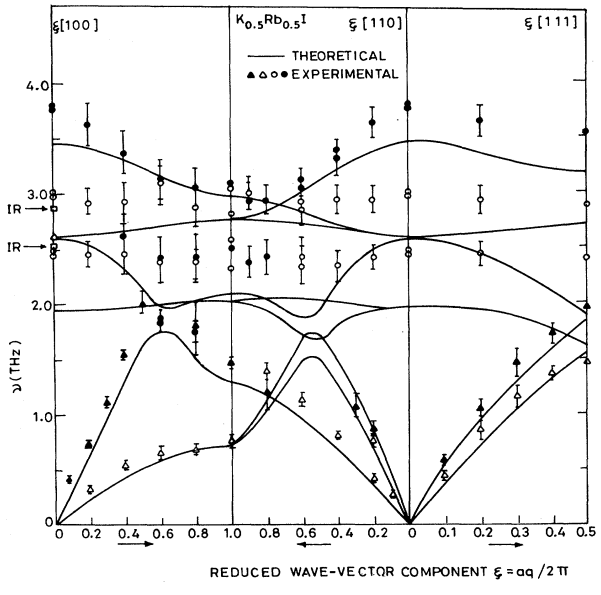

FIG. 1. Phonon dispersion in the mixed crystal $K_{0.5}Rb_{0.5}I$. Circles indicate the experimental inelastic neutron scattering (INS) results of Renker *et al.* (Ref. 16); triangles indicate the INS data of Aslam *et al.* (Ref. 14), and squares indicate the infrared (IR) data of Fertel and Perry (Ref. 4).

CONCLUSIONS

The present simple model is applicable to any mixed system of known structure. In the case of established two-mode behavior shown by III-V mixed compounds, the present model is found to give very good agreement. We intend to publish the results later.

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