Optical phonon frequencies in the quaternary $CdTe_{1-x-y}Se_xS_y$ mixed system

H. C. Gupta, Geeta Sood, Jaishree Malhotra, and B. B. Tripathi
Department of Physics, Indian Institute of Technology, Hauz Khas, New Delhi 110 016, India
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The optical phonon frequencies of the mixed-crystal system $CdTe_{1-x-y}Se_xS_y$ are calculated theoretically by means of a concentration-dependent model utilizing the effect of nonrandomness. The calculations are in satisfactory agreement with the experimental results.

There has been a great interest in the last few years in studying the vibrational spectra of mixed crystals.[1-4] One of the important theoretical approaches used to explain the phonon behavior has been the modified rigid-ion model proposed by Namjoshi, Mitra, and Vetelino.[5] Recently, we have used a concentration-dependent model based on a Green's-function technique utilizing the modified rigid-ion model (MRIM) to study the lattice-dynamical properties of semiconducting ternary $AB_{1-x}C_x$ mixed systems[6,7] and $B_{1-x}C_x$ binary alloys.[8] Particular attention was paid to their phonon spectra in terms of their local or gap mode behavior. Multicomponent mixed crystals have been studied less intensively. However, at present some of them have practical applications; therefore it is important to obtain information concerning the solid-state properties of concrete solid solutions of this type and to elucidate how much the theoretical model applicable to binary and ternary mixed systems may be used for the quaternary mixed system.

The system of mixed crystals under consideration ($CdTe_{1-x-y}Se_xS_y$) is perhaps one of the simplest multicomponent systems. The fact is that all the ternary mixed crystals which are special cases of the quaternary $CdTe_{1-x-y}Se_xS_y$ system ($CdTe_{1-x}Se_x$, $CdTe_{1-y}S_y$, $CdSe_xS_y$) have a so-called two-mode-type[9-11] behavior of the vibtrational spectra with composition. For this reason one might expect bands of the components CdTe, CdSe, and CdS to appear in the spectra of the quaternary $CdTe_{1-x-y}Se_xS_y$ mixed system. Therefore in the present paper we have tried to investigate such behavior in this system.

The components of the $CdTe_{1-x-y}Se_xS_y$ system are CdTe, CdS, and CdSe. Out of these, CdTe occurs in the zinc-blende structure only, whereas CdS and CdSe exist in both the zinc-blende and the wurtzite structure.[12] The local environment of an atom in the two structures, zinc blende and wurtzite, is very similar (tetrahedral coordination). Furthermore, the phonons in compounds with a wurtzite structure have been studied by an equivalent sphalerite (zinc-blende) approximation.[13] Therefore, we have assumed the zinc-blende structure for all the components CdTe, CdS, CdSe in the present study.

We consider a zinc-blende lattice formed by two interpenetrating sublattices numbered 1 and 2 and occupied by four types of atoms A, B, C, and D in a way that corresponds to the situation in the mixed system $AB_{1-x-y}C_xD_y$. Sublattice 1 is occupied by atoms of type A and sublattice 2 is occupied by atoms of types B, C, and D. The dynamical matrix for the multicomponent system $AB_{1-x-y}C_xD_y$, along the similar lines as in ternary $AB_{1-x}C_x$ mixed system,[6,7] can be written as

$$\begin{vmatrix} P-m_A\omega^2 & (1-x-y)Q & xQ & yQ \\ (1-x-y)Q^* & (1-x-y)[(1-x-y)+\lambda_1 x+\lambda_2 y]P-m_B\omega^2 & (1-x-y)x(1-\lambda_1)P & (1-x-y)y(1-\lambda_2)P \\ xQ^* & x(1-x-y)(1-\lambda_1)P^* & x[x+\lambda_1(1-x-y)+\lambda_3 y]P-m_C\omega^2 & xy(1-\lambda_3)P \\ yQ^* & (1-x-y)y(1-\lambda_2)P^* & xy(1-\lambda_3)P^* & y[y+(1-x-y)\lambda_2+x\lambda_3]P-m_D\omega^2 \end{vmatrix}=0 \quad (1)$$

where P and Q are each 3×3 matrices for the zinc-blende structure.[6,7] λ_1, λ_2, and λ_3 are the nonrandomness parameters for the mixed system $AB_{1-x}C_x$, $AB_{1-y}D_y$, and AC_xD_y $(x+y=1)$, respectively, and are introduced in such a way that in a mixed $AB_{1-x}C_x$ system, $(1-x)$ B atoms will interact with $(1-x)$ B atoms as well as $\lambda_1 x$ C atoms; similarly x C atoms will interact with x C atoms as well as with $\lambda_1(1-x)$ B atoms. Along similar lines, the nonrandomness parameters λ_2 and λ_3 are taken into account for the mixed $AB_{1-y}D_y$ and AC_xD_y $(x+y=1)$ crystal system. When both x and y are zero, the dynamical matrix equation (1) reduces to a 2×2 matrix giving the phonon frequencies of the binary (AB) system only. For the sum of x and y $(x+y=1)$ equal to unity the matrix equation (1) reduces to 3×3 matrix giving phonon fre-

TABLE I. Parameters used for the vibrational spectra calculations of $CdTe_{1-x-y}Se_xS_y$ mixed system (a in Å; C_{11}, C_{12}, C_{14} in 10^{11} dyn/cm^2; ω_{LO}, ω_{TO} in cm^{-1}) (Refs. 12, 15–17).

	CdTe	CdSe	CdS
a	3.232	3.02	2.91
Z_{eff}[a]	1.509	2.24	2.12
ε_∞	7.05	6.0	5.9
C_{11}	5.35	7.41	9.07
C_{12}	3.681	4.52	5.81
C_{44}	1.994	1.317	1.504
ω_{LO}	169	210	310
ω_{TO}	139	169	240

[a] Z_{eff} represents the effective charge as calculated by the Lyddane-Sachs-Teller relation.

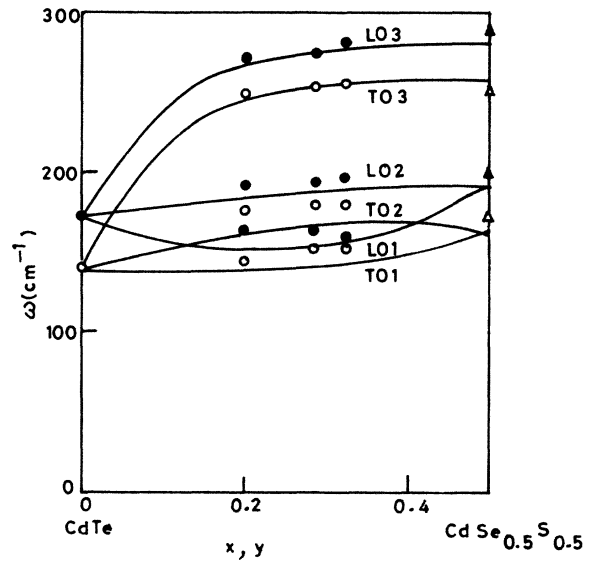

FIG. 1. Concentration dependence of TO and LO vibration frequencies of $CdTe_{1-x-y}Se_xS_y$ mixed crystal for $x=y$. ○,● are the results of Ref. 15; △,▲ are the results of Ref. 9 for TO and LO vibrations, respectively.

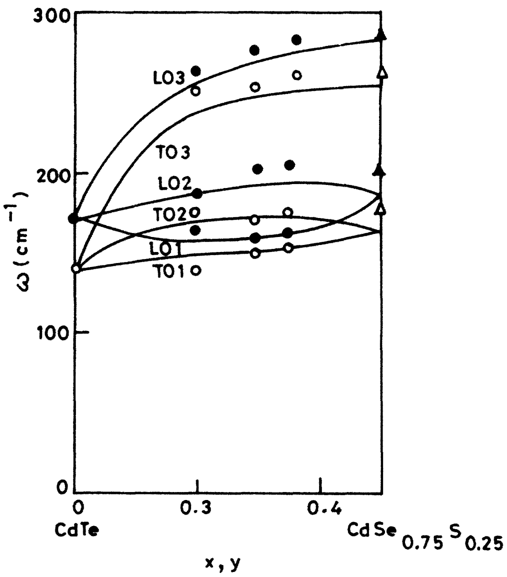

FIG. 2. Concentration dependence of TO and LO vibration frequencies for $CdTe_{1-x-y}Se_xS_y$ mixed crystal for $x=3y$. ○,● are results of Ref. 15; △,▲ are the results of Ref. 9 for TO and LO vibrations, respectively.

quencies of the ternary AC_xD_y system and for other values of x and y the dynamical matrix equation (1) gives phonon frequencies of the quaternary $AB_{1-x-y}C_xD_y$ mixed system.

To investigate the vibrational spectra of the quaternary $CdTe_{1-x-y}Se_xS_y$ system as a function of x and y the values of the constants taken for the binary compounds are listed in Table I. The values of the nonrandomness parameters λ_1, λ_2, and λ_3 for the ternary mixed systems $CdTe_{1-x}Se_x$, $CdTe_{1-y}S_y$, and $CdSe_xS_y$ as a function of x and y are calculated by using one of the optical phonon frequencies of experimental two-mode-type transformation of the vibrational spectra with composition.[9,11] A linear variation of x from Vegard's law[14] has been considered for evaluating the constants for the ternary and the quaternary mixed systems.

The vibrational frequencies of $CdTe_{1-x-y}Se_xS_y$ as a function of concentration x,y at the zone center are displayed in Figs. 1 and 2, respectively, for $x=y$ and $x=3y$. In Fig. 1, for both x and y equal to zero we get only two optical phonon frequencies for the binary system CdTe. For $x=y=0.5$ for the ternary system $CdSe_{0.5}S_{0.5}$ only four optical phonon frequencies are observed and for $0 \leq x \leq y \leq 0.5$, we get six optical phonon frequencies in agreement with the experimental facts.[15] The case for $x=3y$ is similar. In Figs. 1 and 2 we display the experimental points from the far-infrared spectroscopy experiments of Burlakov *et al.*[15] and good agreement has been obtained in both the cases within a discrepancy of the order of 5–6%. From Figs. 1 and 2 one can also detect the bands of the components CdTe (TO1-LO1), CdSe (TO2-LO2), and CdS (TO3-LO3) in accordance with the frequencies given in Table I.

Thus, the concentration-dependent model utilizing the effect of a nonrandomness parameter applicable to the ternary mixed system[6,7] and binary alloy[8] can be satisfactorily applied to the quaternary mixed systems.

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