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Influence of reduced mass differences on the Raman spectra of ternary mixed compounds: $Zn_{1-x}Fe_xS$ and $Zn_{1-x}Mn_xS$

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A Raman scattering study of the mixed crystals $Zn_{1-x}Fe_xS$ and $Zn_{1-y}Mn_yS$ has been carried out for different Fe ($0 \leqslant x \leqslant 0.05$) and Mn ($0 \leqslant y \leqslant 0.5$) concentrations. It is found that both the strengths and the frequencies of the TO and LO modes of ZnS are approximately independent of the Mn (or Fe) concentration. However, as Mn (or Fe) is substituted for Zn, four additional first-order modes with frequencies $\omega(\mathrm{TO}) < \omega < \omega(\mathrm{LO})$ are observed in the Raman spectra. Three of the new modes have frequencies equal to those of sharp peaks in the density of states of ZnS and thus they are attributed to resonance or band modes. Another extra mode, with frequency at 323 cm^{-1}, is observed in samples with $x \geqslant 0.10$, and it is assigned to a breathing mode of the nearest-neighbor sulfur atoms around Mn atoms. The observation of such extra features does not correspond to the usual behavior observed in other ternary mixed crystals where either one-, two-, or mixed-mode behavior is observed. Conversely, it is found that the measured frequencies of all the new peaks are nearly constant, independent of the Fe or Mn concentration. This "frozen-mode" behavior is believed to occur because of the small reduced mass difference between the binary end members when the Zn atoms are replaced by either Fe or Mn. More specifically it is suggested that the frozen-mode behavior will occur whenever the reduced mass difference between the end pairs ($\Delta\mu$) is less than or equal to approximately 2.0 amu. It appears that consideration of the reduced mass difference may also be used to delineate between one- and two-mode behavior. That is, the available data suggest that one-mode behavior occurs in samples with $2 \lesssim \Delta\mu \lesssim 7$ and two-mode behavior in samples with $\Delta\mu \gtrsim 7$.

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I. INTRODUCTION

The addition of impurities to diatomic polar crystals can, ideally, enable one to modify the structural, vibrational, and optical properties of the host crystal in a controlled manner. This is important if one wishes to fully realize the technical potential of compounds such as II-VI semiconductors. The inclusion of dopants can also lead to new effects that are of fundamental interest. For example, the optical and vibrational properties of dilute-magnetic semiconductors that are obtained by doping II-VI semiconductors with Mn or Fe, have been widely studied.[1,2] In a more general context the lattice dynamics of ternary mixed crystals have revealed a variety of interesting phenomena.[3–5] These include the occurrence of so-called one-mode or two-mode behavior, as well as intermediate mixed-mode systems. Another type of behavior is also observed, in which several new resonance or band modes occur in the Raman spectra of the mixed compounds. Considerable effort has been expended[3,4] to determine criteria that would enable one to predict *a priori* the type of behavior one might expect in a given system. Most of these are based on the various masses of the constituents of the mixed compound and/or the polarity of the end members. Although considerable progress has been made, several systems exhibit behaviors that represent exceptions to the existing criteria. In this paper we will present results obtained on two such systems.

We have carried out an investigation of the effects of Mn and Fe substitution on the vibrational properties of ZnS. The crystalline lattice dynamics of zinc sulphide (ZnS) have been studied in the past from both the experimental[6–8] and theoretical[9] points of view and thus we can consider the vibrational spectrum of pure ZnS to be relatively well known. The vibrational spectrum of the mixed compound has also been investigated previously using Raman scattering spectroscopy and previous work includes detailed studies[10–12] of the first- and second-order Raman spectra of ZnS, which thus simplifies the detection of modifications induced by the impurity atoms. Raman scattering studies of the effects of adding relatively small concentrations of magnetic atoms to ZnS have been carried out by a few groups.[4,13] They found that new modes, all with frequencies in the range $\omega(\mathrm{TO}) < \omega < \omega(\mathrm{LO})$ appeared in their spectra when a small amount ($\approx 1\%$) of a magnetic impurity such as Fe, Mn, Co, or Cr, was added to ZnS. Zigone *et al.*[4] found that the frequencies of the new modes were approximately the same for each of the five different impurities they studied. They also found that the frequency variation of the new modes with pressure was similar to that of the LO(Γ) mode, and smaller than that of the TO(Γ) mode. On the basis of these results the new modes were assigned to resonance modes.[4] In this paper we will extend these earlier studies by examining the effects associated with much larger impurity concentrations.

Raman spectra have been obtained from the semimagnetic alloys $Zn_{1-y}Mn_yS$, with $y=0.01$, 0.02, 0.03, 0.10, 0.20, 0.35, and 0.50, and $Zn_{1-x}Fe_xS$, with $x=0.02$ and 0.05. It is shown, that, in contrast to most other mixed crystals, the frequency of the Raman active modes of the ZnS host remained basically unaltered (“frozen modes”) even for large impurity concentrations. Moreover, the frequencies of four additional features that are observed in the spectra of $Zn_{1-x}Fe_xS$ and $Zn_{1-x}Mn_xS$, are also independent of impurity concentration. However, the intensity of the new modes increases as the dopant concentration increases. It should also be noted that the frequencies of three of the impurity induced modes can be closely correlated with peaks in the density of states of ZnS. The observation of a frozen-mode behavior is not consistent with the more usual one-, two-, or mixed-mode behavior[3] that is observed in many mixed crystals. The observations presented in this paper have led us to propose an empirical mass criterion, as described below, that may be used to predict the occurrence of frozen-mode behavior.

II. RAMAN SPECTRA OF MIXED CRYSTALS

The study of mixed crystals has led to the observation, and definition, of predictable patterns of behavior that are pertinent to systems such as $AB_{1-x}C_x$. If one observes the so-called one-mode behavior, the LO and TO modes of *AB* change continuously into the LO and TO modes of *AC*, with the modes having approximately the same intensity throughout the complete range.

On the other hand, if two-mode behavior is observed, the modes of both the end products (*AB* and *AC*) appear together throughout much of the mixed range. In this case the intensity of the modes are roughly proportional to the concentration of their parent compound. Chang and Mitra[3] summarized these observations with the relations

$$M_B<\mu_{AC} \text{ if } \mathrm{M}_B<M_C [\text{or } M_C<\mu_{AB} \text{if } M_B>M_C]. \tag{1}$$

Here μ_{AC} and μ_{AB} are the reduced masses of the compounds *AC* and *AB*, respectively. Chang and Mitra found that if Eq. (1) was obeyed two-mode behavior was observed; otherwise one-mode behavior was assumed to prevail.

The above criteria are obviously not adequate to address the situations, such as those represented by $Zn_{1-x}Mn_xS$, when several new modes appear in the spectrum and thus neither single-mode or two-mode behavior, or even a combination of the two (mixed-mode behavior), occurs. It appears that the observation of several impurity-induced modes can be attributed to one of two other distinct scenarios.[4,5] For example, one can have local modes associated with the impurity atom that are in resonance with modes of the host crystal and these give rise to what are called resonance modes in the spectra. The amplitudes of resonance modes are enhanced near the defect, but the modes may propagate through the lattice and should give rise to relatively broad peaks in the spectrum.

Finally there is another possibility. The addition of impurities, particularly in large concentrations, can be viewed as creating disorder in the host crystal. In this case, crystal momentum is no longer conserved, and $q\neq 0$ phonons can appear[4,5,14,15] in the Raman spectra. These types of impurity-induced modes have been designated as band modes. Such modes appear as new peaks in the spectra whose energy can be closely correlated with peaks in the density of states of the host crystal. This mechanism appears to be favored in those situations in which the bond strengths of the host crystal are large. Our results also suggest that consideration of the reduced mass difference between the end pairs; that is, $\mu_{AC}-\mu_{AB}$, leads to an overriding condition and we propose that frozen-mode behavior should be observed in all samples for which

$$\Delta\mu=|\mu_{AB}-\mu_{AC}|\lesssim 2. \tag{2}$$

III. EXPERIMENTAL DETAILS

The $Zn_{1-x}Fe_xS$ and $Zn_{1-y}Mn_yS$ crystals used in our experiments were grown by the vapor transport technique employing the corresponding binary compounds in each case and using iodine as the transport agent. In the case of $Zn_{1-x}Fe_xS$ it was not possible to grow good-quality crystals for $x>0.05$. This is consistent with previous workers[16] who found that the range of *x* for which Fe can be introduced into ZnS is considerably less than in the case of Mn, when using vapor transport techniques.

The samples were characterized using x-ray diffraction and the resulting patterns revealed that the samples had the cubic zinc-blende structure. For this structure the symmetry of lattice vibrations can be used to classify them according to the irreducible representations of the T_d point group: The phonons are then designated[5] as A_1 (or Γ_1), E (or Γ_{12}), or F (or Γ_{15}).

Room-temperature Raman-scattering measurements were carried out in a Labram Dilor spectrometer where a He-Ne laser beam was utilized to excite the sample through the 50 ×objective of a confocal microscope. This allowed us to focus the laser beam to a spot of approximately two microns in diameter and thus verify the crystal homogeneity by obtaining spectra from different positions on the sample. The scattered light was collected and analyzed with a thermoelectrically cooled charge-coupled device (CCD) interfaced to a computer.

IV. RESULTS

A. $Zn_{1-x}Fe_xS$

Figure 1 shows the room-temperature Raman spectra of $Zn_{1-x}Fe_xS$ with iron concentrations $x=0$, $x=0.02$, and $x=0.05$. In the spectra obtained from the Fe-doped samples three prominent peaks appear in the spectral region between the TO (276 cm^{-1}) and LO (350 cm^{-1}) phonons. The three lines appear at 300 (Y_1), 312 (Y_2), and 332 cm^{-1} (Y_3) in

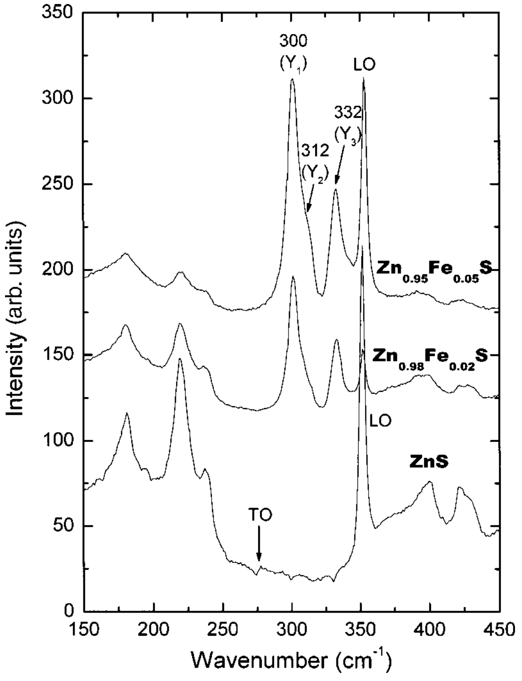

FIG. 1. Room-temperature Raman spectra of pure ZnS and of $Zn_xFe_{1-x}S$. The spectra have been displaced vertically for clarity. The doping-induced features are indicated as Y_1, Y_2, and Y_3.

both samples, in good agreement with previous measurements on samples with small Fe concentrations.[4,13] The bands appearing below 250 cm^{-1} correspond to second-order modes not relevant for the present discussion. Polarized measurements (not shown) indicated that Y_1 exhibited $\Gamma_1+\Gamma_{15}$ symmetry, while the appearance of Y_2 and Y_3 was consistent with Γ_{15} symmetry. These symmetry assignments are also in accord with previous determinations.[4,13] It is important to note that: (i) the frequency of the TO and LO modes of ZnS remain constant, independent of the Fe concentration x; (ii) the relative intensities of the extra modes increases with increasing Fe concentration, and; (iii) the frequency of the three additional, doping-induced modes remain constant, independent of the iron concentration.

Thus for the $Zn_{1-x}Fe_xS$ cases discussed here ($x=0.02$ and 0.05), we can conclude that the observed behavior does not conform to the one-, two-, or mixed-mode behavior normally observed in other II-VI-based mixed crystals. It is interesting to consider this result in the context of the properties of the two end products. Unfortunately very little data are available on the optical properties of FeS. To get an approximate estimate of the relevant quantities we carried out infrared reflectivity measurements on a pressed pellet of FeS powder. Although the spectrum was not of high quality the measurements revealed a weak Restrahlen band and fits to the spectra yielded $\omega_{TO}\approx 128$ and $\omega_{LO}\approx 148\ cm^{-1}$. Raman spectra obtained from the same powder had strong peaks at 53, 88, 148, 156, 214, 220, 467, and 473 cm^{-1}. There is no evidence of a mode at 128 cm^{-1} in the region of the Raman spectrum between 88 and 148 cm^{-1}. However, one should note that the TO mode of ZnS is also absent, or very weak, in many of the spectra shown in Figs. 1 and 2. In addition, the fits to the infrared reflectivity must be considered tentative given the relatively poor quality of the spectra. We will thus assume that $\omega_{LO}\approx 148\ cm^{-1}$ and that $88<\omega_{TO}<128\ cm^{-1}$. Given these frequencies it is clear that the Resthrahlen regions of ZnS and FeS are well separated and one might expect two-mode behavior. As Chang and Mitra[3] have shown, however, the criterion given by Eq. (1) is much stronger and according to this criterion $Zn_{1-x}Fe_xS$ should exhibit one-mode behavior. Obviously this is not the case either, since there are too many extra modes in the spectra and because the LO and TO frequencies are independent of doping.

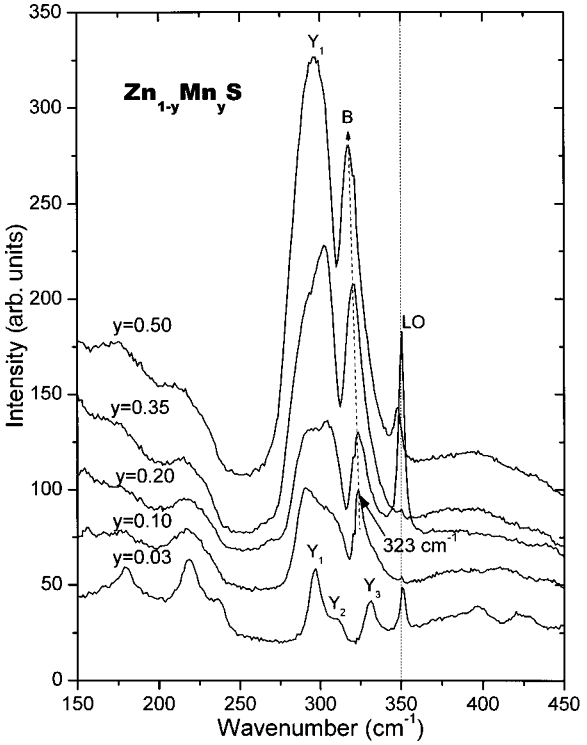

FIG. 2. Room-temperature Raman spectra of $Zn_xMn_{1-x}S$ for the indicated Mn concentrations. The doping-induced features are indicated as Y_1, Y_2, Y_3, and B. The spectra have been displaced vertically for clarity.

As to the latter point, one might argue that five atomic percent of iron might not be enough to cause measurable changes to the ZnS vibrational modes. However, in the case of another zinc chalcogenide, $Zn_{1-x}Mn_xTe$, a shift of 3 cm^{-1} is measured for the LO frequencies when $x=0.05$, which is certainly observable. In spite of this, however, these observations raise the question as to whether crystals with higher impurity concentrations might present evidence of a more usual type of behavior—for example, that observed in mixed crystals based on zinc tellurides[17] or selenides.[2] In an attempt to address this question Raman-scattering experiments have been carried out in $Zn_{1-y}Mn_yS$ crystals with y values in the 0.01–0.50 range. Mn was chosen for these experiments (i) because it is easily incorporated into the ZnS host and (ii) because Mn and Fe are neighbors in the periodic table and therefore have similar atomic masses. The results of such experiments are presented and discussed below.

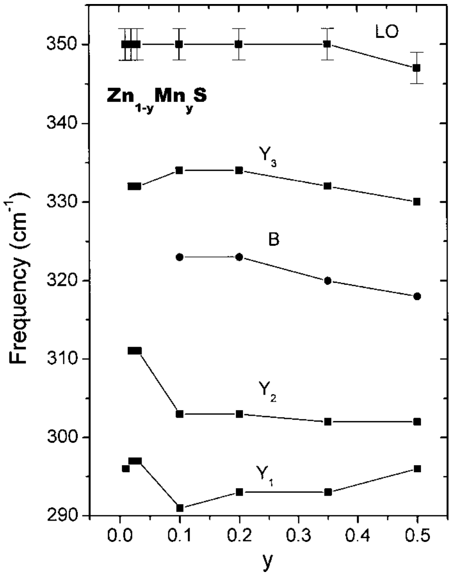

FIG. 3. Frequency variation of the Raman modes observed in the spectra of the $Zn_xMn_{1-x}S$ samples as a function of Mn composition.

It should be mentioned that attempts to correlate the additional features in the Raman spectra of $Zn_{1-x}Fe_xS$ with the Raman modes of FeS and FeS_2 were not successful. The characteristic modes of FeS (Ref. 18) at 472 cm^{-1} and of FeS_2-marcasite[19] at 386 and 323 cm^{-1} were not observed. In the case of FeS_2-pyrite Ushioda[20] reported phonons at 351, 386, and 443 cm^{-1} while in the Raman spectrum of pyrite films, de las Heras *et al.*[21] measured phonons at 341, 377, and 427 cm^{-1}. Moreover, we carried out micro-Raman experiments in FeS and FeS_2 powders. For FeS we obtained strong peaks at 53, 88, 148, 156, 214, 220, 467, and 473 cm^{-1}. In the case of FeS_2 the Raman modes were observed at 343, 379, and 429 cm^{-1}, in agreement with the reported data of de las Heras *et al.*[21] None of these features correlate with the modes observed in our samples of $Zn_{1-x}Fe_xS$.

B. $Zn_{1-y}Mn_yS$

Raman-scattering experiments were carried out on $Zn_{1-y}Mn_yS$ crystals with $y = 0.01$, 0.02, 0.03, 0.10, 0.20, 0.35, and 0.50. The room-temperature Raman spectra of five $Zn_{1-y}Mn_yS$ samples are shown in Fig. 2. The spectra shown were obtained by using a He-Ne laser for which the intensity of the TO mode is very weak and difficult to observe. The low intensity of the LO mode in the $y = 0.10$ sample was probably due to a scattering geometry effect, where we could have been measuring on a crystalline plane from which observation of the LO mode is forbidden such as the (1 1 0) surface. Although the $Zn_{1-y}Mn_yS$ crystals were unoriented, it was possible to observe partial polarization effects and resolve the broad features in the spectra by performing polarized experiments. The frequencies of the different lines in the spectra are summarized in Fig. 3. From these one may observe that the frequency variations are surprisingly small considering the changes in sample composition. Another interesting observation in Fig. 3 is the fact that the frequency of the LO mode remains constant for manganese concentrations of up to 35% and softens only two wave numbers when half of the zinc atoms have been substituted for manganese atoms. This is an indication that, as in the case of $Zn_{1-x}Fe_xS$, the effect of impurities on the Raman spectra of ZnS is accommodated by the host through the appearance of the additional modes Y_1, Y_2, Y_3, and of yet another mode at 323 cm^{-1}, which appears for $x \geqslant 0.10$ (Fig. 2).

These results are thus similar to those found in ZnFeS in that the new, doping-induced modes have frequencies within the range defined by the TO and LO modes of ZnS, and that their frequencies are essentially independent of dopant concentration. It is also clear that neither one-, two-, or mixed-mode behavior can be used to describe the results. Instead there is a different behavior, one in which the impurity-induced modes appear to be "frozen," in the sense that the vibrational frequencies of the Raman active modes do not exhibit significant variations as a function of doping. There are, however, variations in the relative intensities and linewidths of the observed peaks (Fig. 2). Clearly, the peaks become broader with increasing Mn concentration, presumably as a consequence of the disorder introduced by the incorporation of Mn atoms into the ZnS lattice.

Other authors have also observed additional Raman modes in the spectra of ZnS containing low concentrations of transition-element substitutional impurities.[4,13,22–24] Zigone *et al.*[4] carried out a detailed analysis of the Raman spectra of ZnS where various transition-element (Cr, Mn, Fe, Co, and Ni) impurities were present at concentrations of the order of 1%. They observed additional features at frequencies similar to those found here. Based upon the results of Raman-scattering experiments under pressure and numerical calculations employing a Green's-function model which considered impurity-host bonding and phonons in a rigid-ion model, they concluded that the observed features could be ascribed to resonant modes, as opposed to band modes. Such resonant modes are expected to have a large amplitude in the vicinity of the defect but, in contrast to local modes, may propagate through the crystal, and should have relatively broad linewidths. Band modes are activated by disorder through wave vector nonconservation and may produce spectra related to the single phonon density of states. In this case the identification of the modes by Zigone *et al.*[4] was a subtle point since the spectra of ZnS, with impurities present, show a remarkable similarity with the features of the one-phonon density of states,[6] as illustrated in Fig. 4. Given that the impurity-induced modes are also quite narrow, as are the sharp features in the density of states, one might argue that Y_1, Y_2, and Y_3 correspond to band modes. Such a designation would also appear to be consistent with the observation that the frequencies of these modes are independent of the impurity mass, although this would be a small effect in the present case. It is interesting to note that spectra obtained on a similar alloy such as $Zn_{1-x}Mn_xTe$ (Ref. 18) do not appear to show a related behavior. The Raman spectra of $Zn_{1-x}Fe_xSe$,[2] however, do contain features whose frequencies correspond well to the frequencies at which peaks occur in the corresponding density of states.

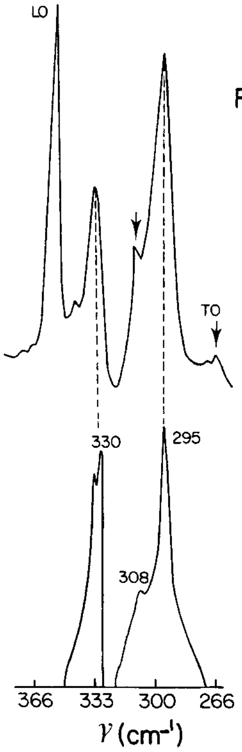

FIG. 4. Comparison between the Raman spectrum of the $Zn_{0.95}Fe_{0.05}S$ sample and the ZnS one phonon density of states.

V. DISCUSSION

A. Agreement with existing models

The Raman spectra of the zinc chalcogenides and of some gallium-based semiconductors have been studied by Kunc and Bilz.[25] Their analysis was based on the overlap shell model which is characterized by a positive shell charge simulating the polarization of overlap charges. It is indicated in that work that, in general, the lighter or more polarizable ions show stronger scattering than heavier or less polarizable ions, and that the influence of the ion mass ratio dominates over the influence of ionic polarizabilities. This is consistent with the conclusions of Chang and Mitra,[3] who found that their mass criterion [Eq. (1)] was the dominant factor in resolving questionable cases. On the other hand, if one applies this criterion [Eq. (1)] to $Zn_{1-x}M_xS$ (M = Fe, Mn) it predicts that one-mode behavior should be observed in both cases, which is in obvious disagreement with the experimental results. It is also interesting to note that for the zinc-blende form of MnS the optical phonons are found[26,27] at $\omega_{TO} = 286\ \mathrm{cm}^{-1}$ and $\omega_{LO} = 343\ \mathrm{cm}^{-1}$ and the band gap is $E_g \approx 3.6$ eV. These parameters are similar to those of ZnS and on this basis one would also expect[3] to observe one-mode behavior in ZnMnS. Recall that for ZnFeS the Restrahlen bands of the end members are well separated and on this basis two-mode behavior is expected. However, both mixed compounds exhibit a similar behavior that differs from both of these more commonly accepted scenarios.[28,29] It thus appears that none of the current criteria developed to predict the phonon behavior in mixed crystals even consider a quasistatic dependence of the phonon frequencies such as we have observed in $Zn_{1-x}M_xS$ (M = Fe, Mn).

B. Consideration of reduced mass difference of end members ($\Delta\mu \lesssim 2$)

Table I shows the difference $\Delta\mu$, Eq. (2), for various II-VI-based mixed crystals and Table II for some III-V-based alloys. For the compounds studied here one should note that for $Zn_{1-x}Fe_xS$ the effective masses of the end members are remarkably similar ($\mu_{ZnS} = 21.51$ amu, $\mu_{FeS} = 20.37$ amu) having a difference of 1.14 amu. In the case of $Zn_{1-x}Mn_xS$ this difference is 1.27 amu. In fact, if one carries out the same exercise for other mixed crystals, such as those based on II-VI, III-V, and I-VII compounds, it is found that a trend exists in the sense that mixed crystals $AB_{1-x}C_x$ whose effective mass difference $\Delta\mu = |\mu_{AC} - \mu_{AB}|$ is relatively small exhibit one-mode behavior, while those with larger $\Delta\mu$ values exhibit two-mode behavior. This observation highlights the relevance of the physical quantity $\Delta\mu$, which may be considered an important parameter for the vibrating ternary system. The usefulness of comparing the effective masses of the end members in mixed crystals has been already pointed out by Elliot *et al.*[30] who proposed a criterion based on the coherent potential approximation for crystals of the type $A_xB_{1-x}C$. For two-mode behavior they obtained the condition

$$\left|1 - \frac{\mu}{\mu'}\right| > \frac{\varepsilon(0) - \varepsilon(\infty)}{\varepsilon(0) + \varepsilon(\infty)}, \tag{3}$$

where the primed variable indicates the effective mass value of the minor binary component. However, if one applies relation (3) to the cases of $Zn_{1-x}M_xS$ (M = Fe, Mn), it is found that the system should present one-mode behavior. It is interesting to note that the difficulty of applying Eq. (3) when $\mu \cong \mu'$, which is the situation in $Zn_{1-x}M_xS$ (M = Fe, Mn). We would argue that the empirical criterion proposed in Eq. (2) should be considered to be dominant over Eq. (3).

The Raman spectra of $Zn_{1-x}Ni_xS$, $Zn_{1-x}Co_xS$,[13,22] and $Zn_{1-x}Cr_xS$ (Ref. 4) also present additional modes with frequencies similar to those reported in this work. In these three cases the values of $\Delta\mu$ are 0.77, 0.75, and 1.68 amu. In Ref. 24 it is noted that no additional modes appeared in the Raman spectra of $Zn_{0.97}Ti_{0.03}S$ ($\Delta\mu = 2.31$ amu) within the TO-LO range. Assuming that the absence of the additional lines between the TO and LO modes for a particular crystal composition is an indication that the frozen-mode behavior will be absent for a wide range of concentrations, then, from the values in Tables I and II and from the current available data, one may tentatively assume that if $\Delta\mu \leqslant f$, where $f \approx 2.0$ amu, frozen-mode behavior should be observed. This condition is satisfied if the mass of atom B is close enough to that of atom C. Therefore, from the lattice mechanics point of view, the frequencies of the vibrational modes should not vary significantly between those of a pair AC vibrating with effective mass μ_{AC} and those of a pair AB vibrating with effective mass μ_{AB}, provided that there is not an abrupt change in the chemical bond (force constant) when atoms C substitute for atoms B.

TABLE I. Observed mode behavior (column 8) of II-VI-based mixed crystals ($AB_{1-x}C_x$) compared to the Chang-Mitra mass criterion (CMMC) of Eq. (1) (column 7) and to the effective mass difference of the end members (column 9).

$AB_{1-x}C_x$	m_A	m_B	m_C	μ_{AB}	μ_{AC}	CMMC [Eq. (1)]	Observed mode	$\Delta\mu=\lvert\mu_{AB}-\mu_{AC}\rvert$
SZnMn	32	65.37	54.95	21.48	20.22	1	Frozen (this work)	1.26
SZnFe	32	65.37	55.85	21.48	20.34	1	Frozen (this work)	1.14
SZnNi	32	65.37	58.69	21.44	20.71	1	Frozen (Refs. 13 and 22)	0.73
SZnCo	32	65.37	58.93	21.48	20.74	1	Frozen (Refs. 13 and 22)	0.74
SZnCr	32	65.37	52	21.48	19.81	1	Frozen (Ref. 4)	1.67
SeZnCo	79	65.37	58.93	35.66	33.75	1	Two (Ref. 2), frozen?	1.91
SeZnFe	79	65.37	55.85	35.66	32.72	1	Two (Ref. 2), frozen?	2.94
SZnCd	32	65.37	112.4	21.51	24.94	1	One (Refs. 34, 35, and 36)	3.43
TeZnMn	127.6	65.37	54.95	43.23	38.41	1	Two (Ref. 17)	4.82
ZnSeTe	65.37	78.96	127.6	35.76	43.23	1	One (Ref. 37)	7.46
SeCdZn	78.96	112.4	65.37	46.38	35.76	1	One (Ref. 38), intermediate (Ref. 39)	10.62
CdSeTe	112.4	78.96	127.6	46.38	59.76	1	Two (Ref. 40)	13.38
SeCdMn	79	112.4	54.95	46.38	32.4	1	Two (Ref. 39)	13.98
ZnSeS	65	79	32	35.66	21.44	2	Two (Ref. 41)	14.22
TeZnCd	127.6	65.37	112.4	43.22	59.76	1	Two (Ref. 42)	16.54
SeZnMg	79	65.37	24.3	35.76	18.58	2	Two (Ref. 43)	17.17
TeHgCd	127.6	200.6	112.4	78.0	59.76	1	Two (Ref. 44)	18.24
TeCdMn	127.6	112.4	54.95	59.76	38.4	2	Two (Ref. 32)	21.36
CdSeS	112.4	79	32	46.6	24.9	2	Two (Refs. 45 and 46)	21.5
SnSSe	118.7	32	79	25.2	47.4	2	Two (Ref. 47)	22.2
TeZnMg	127.6	65.37	24.3	43.2	20.4	2	Two (Ref. 48)	22.8
TeMgCd	127.6	24.3	112.4	20.4	59.76	2	Two (Ref. 33)	39.36

Finally, one should note that SeZnCo and SeZnFe appear to represent exceptions to the trend we have identified in that they have $\Delta\mu\approx 2$ and yet their spectra have been interpreted in terms of two-mode behavior. *A priori* one might simply argue that these samples should be eliminated from consideration on the basis that the end members FeSe and CoSe do not exist[2] and therefore any predictions based on their reduced masses might be suspect. We would like to point out, however, that, given the data in Ref. 2 another interpretation is, perhaps, possible. For example the impurity induced LO_2 feature observed in that work occurs at the same frequency as a peak in the one-phonon density of states.[31] In addition, this frequency, as well as the host ZnSe frequencies (labeled LO_1 and TO_2) remain approximately constant as the impu-

TABLE II. Observed mode behavior (column 8) of III-V-based mixed crystals ($AB_{1-x}C_x$) compared to the Chang-Mitra mass criterion (CMMC) of Eq. (1) (column 7) and to the effective difference of the end members (column 9).

$AB_{1-x}C_x$	m_A	m_B	m_C	μ_{AB}	μ_{AC}	CMMC [Eq. (1)]	Observed mode	$\Delta\mu=\lvert\mu_{AB}-\mu_{AC}\rvert$
PInGa	30.9	114.8	69.7	24.34	21.40	1	One (Ref. 49), two (Ref. 50), modified (Ref. 51)	2.93
PGaAl	30.9	69.7	26.9	21.40	14.38	1	Two (Refs. 52 and 53)	7.02
GaAsSb	69.7	74.9	121.75	36.10	44.32	1	Two (Ref. 54), mixed (Ref. 55)	8.22
AsGaIn	74.9	69.7	114.8	36.10	45.32	1	Two (strained) (Ref. 56), mixed (Ref. 57)	9.22
PInAl	30.9	114.8	26.9	24.34	14.38	1	Two (Ref. 58)	9.96
InAsSb	114.8	74.9	121.75	45.32	59.08	1	Mixed (Ref. 57)	13.76
GaPAs	69.7	30.9	74.9	21.40	36.10	2	Two (Ref. 59)	14.69
SbGaIn	121.75	69.7	114.8	44.32	59.08	1	Mixed (Ref. 60)	14.76
AsAlGa	74.9	26.9	69.7	19.79	36.10	2	Two (Refs. 61 and 62)	16.31
InPAs	114.8	30.9	74.9	24.34	45.32	2	Two (Refs. 63, 64, and 65)	20.98
SbAlGa	121.75	26.9	69.7	22.03	44.32	2	Two (Ref. 66)	22.29
GaPSb	69.7	30.9	121.75	21.40	44.32	2	Two (Ref. 67)	22.91
AsAlIn	74.9	26.9	114.8	19.79	45.32	2	Two (Ref. 68)	25.53
InPSb	114.8	30.9	121.75	24.34	59.08	2	Two (Ref. 67)	34.74

rity concentration is increased. Thus it appears possible to consider these compounds as "border line" frozen-mode systems. This assignment would be consistent with the reduced mass difference limits we have proposed for such behavior.

In summary, ZnS-based mixed crystals are favorable materials for the frozen-mode behavior to occur since: (i) the frequencies of the TO and LO modes are relatively large (strong bonds), (ii) there is a large LO-TO splitting evidencing large polarity, (iii) the dispersion curves are flat near the high-symmetry points Γ, X, W, and L of the Brillouin zone which produces sharp and well defined peaks in the density of states, (iv) the second-order scattering of phonons with frequency between the TO and LO modes is negligible, and (v) the low mass of the sulphur atom is usually the dominant factor when the effective masses of the end members are computed. Moreover, in accordance with the effective mass criterion mentioned above and with the reported experimental data in Zn$_{1-x}$Cr$_x$S, Zn$_{1-x}$Ni$_x$S, and Zn$_{1-x}$Co$_x$S we believe that the frozen-mode behavior should describe the lattice dynamics of such mixed crystals in a wider range of transition-metal concentrations than those currently reported.

C. Samples with $\Delta\mu \gtrsim 2$

If we now direct our attention to those compounds in Table 1 that have $\Delta\mu > 2$ we note that for those with $2 < \Delta\mu \lesssim 7$ we find that in general one-mode behavior is observed. We would thus like to suggest this might lead to the adoption of such a criterion; namely that if $2 < \Delta\mu \lesssim 7$ we should expect one-mode behavior. The only exception to this proposal is TeZnMn ($\Delta\mu = 4.82$) which experimentally has been found[17] to exhibit two-mode behavior. This result is in defiance of both the Mitra criterion [Eq. (1)] and the reduced mass criterion proposed here. If we now move to the lower members in Table 1 ($\Delta\mu \gtrsim 7$) it appears that two-mode behavior is universally observed. We would thus again suggest that this observation be adopted as an empirical criterion; namely we should expect two-mode behavior in those compounds for which the reduced mass difference of the end members $\Delta\mu > 7$. Note that this results in much better agreement with experiment than does the Mitra mass criterion.

VI. B MODES

Finally, we would like to discuss the mode at 323 cm^{-1} which was evident in the Zn$_{1-x}$Mn$_x$S samples for $x \geqslant 0.10$ (Fig. 2). The frequency of this mode remains constant and its intensity increases as the manganese concentration is increased. A similar mode was reported by Zigone *et al.*[4] at 328 cm^{-1} whose theoretical model was able to reproduce phonons at frequencies similar to those of the Y modes (Fig. 3), but could not account for the 328-cm^{-1} mode which remained unexplained. It is noticed that the 323-cm^{-1} mode lies within the gap of the phonon frequency distribution (Fig. 4), and that its behavior is similar to that of the so-called B mode reported for mixed crystals such as Zn$_{1-x}$Mn$_x$Te,[18] Cd$_{1-x}$Mn$_x$Te,[32] Zn$_{1-x}$Co$_x$Se, and Zn$_{1-x}$Fe$_x$Se (Ref. 20) in the sense that its intensity increases, while its frequency remains constant with increasing Mn content. The frequency of the B mode does, however, have a magnitude that strongly depends on the type of chalcogen atom involved in the crystal composition. In Ref. 36 it is mentioned that a similar mode was reported before at 118.8 cm^{-1} in Cd$_{1-x}$Mg$_x$Te, however, in an earlier paper Nakashima *et al.*[33] pointed out that the temperature dependence of the 118.8-cm^{-1} mode indicated that it was a second-order Raman band. In our case, the low-temperature Raman measurements showed that the mode at 323 cm^{-1} is not a second-order mode.

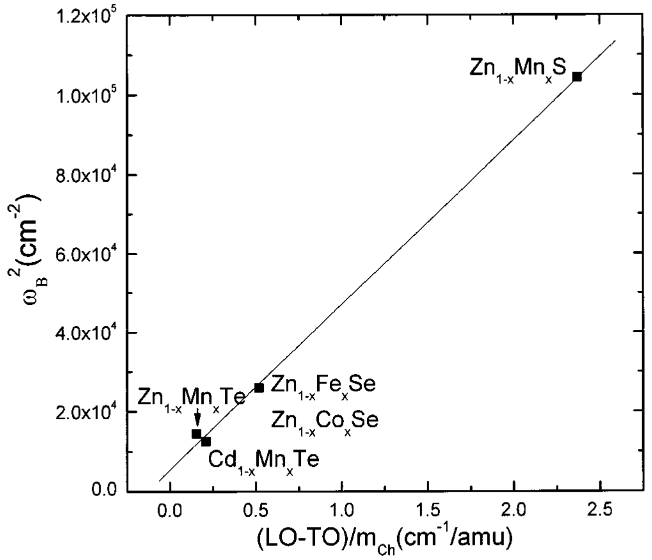

FIG. 5. Squared frequency of the reported B modes (Zn$_{1-x}$Mn$_x$Te, Cd$_{1-x}$Mn$_x$Te, Zn$_{1-x}$Fe$_x$Se, and Zn$_{1-x}$Co$_x$Se) and of the B mode determined in this work (Zn$_{1-x}$Mn$_x$S) as a function of the LO-TO splitting of the II-VI host divided by the atomic mass of the chalcogen atom.

B modes have been interpreted as breathing modes of the nearest-neighbor chalcogen atoms around an impurity atom which remains immobile. The intensity of such a mode must then be proportional to the impurity concentration, which indeed is observed experimentally. In addition, it is expected that the frequency of the mode would be independent of the mass of the impurity and determined basically by the interactions with its surrounding atoms. The strength of those interactions must be strongly dependent on the polarization field surrounding the chalcogen-impurity pair. A quantity that reflects the intensity of such a field is the LO-TO splitting of the II-VI host. In addition, since for B modes it is speculated that the chalcogen atoms move around the impurities in a breathinglike pattern, the squared frequency of these modes (ω_B^2) should scale, if one assumes a harmonic-oscillator-type motion, as $1/m_{\mathrm{Ch}}$ where m_{Ch} is the chalcogen atom mass. In Fig. 5 we have taken into account these two factors and plotted ω_B^2 vs the magnitude of the LO-TO splitting of the II-VI host divided by m_{Ch}. The linear relationship obtained shows that, for the currently available data, B modes are indeed consistent with a picture of moving chalcogen atoms in the polarization field of the II-VI host crystal.

VII. CONCLUSIONS

We have carried out a Raman-scattering study on Zn$_{1-x}$Fe$_x$S, with $x = 0.02$, 0.05, and on Zn$_{1-y}$Mn$_y$S with y

$=0.01$, 0.02, 0.03, 0.10, 0.20, 0.35, and 0.50. It was observed that the inclusion of Fe and Mn atoms within the ZnS lattice caused the appearance of four additional modes between the LO and TO modes of ZnS in the Raman spectra of the ternary alloys. The spectrum of additional lines does not correspond to the more conventional behavior[3] observed in other mixed crystals where the one-, two-, or mixed-mode behavior is generally encountered. The impurity-induced modes at 300, 312, and 332 cm^{-1} were identified with the similar modes observed and studied by Zigone *et al.*[4] and classified as resonance modes. However, based upon the existence of appropriate peaks in the density of states of ZnS, the narrowness of the impurity-induced lines, and the fact that their frequency is independent of impurity mass we suggest that band modes might be a more appropriate assignment. An additional mode at 323 cm^{-1} was observed to follow a behavior similar to the so-called *B* modes (a breathing mode associated with the vibrations of the nearest-neighbor chalcogen atoms around the immobile impurity atoms).

A remarkable characteristic of the six first-order peaks observed in our Raman spectra in the interval $\omega_{\mathrm{TO}} \leqslant \omega \leqslant \omega_{\mathrm{LO}}$, namely the LO, TO, and the four additional lines, was the fact that their frequency did not vary significantly with changes in the impurity concentration. This frozen-mode behavior appears to occur in ternary mixed compounds which have a relatively small difference between the reduced masses of the end members. More specifically, from an analysis of the current data in mixed crystals it is suggested that frozen-mode behavior should occur in those compounds for which the absolute value of the reduced mass difference of the end members ($\Delta\mu$) is less than approximately 2.0 amu. This empirical criterion suggests that frozen-mode behavior should also occur in compounds such as $\mathrm{Zn}_{1-x}\mathrm{Co}_x\mathrm{S}$, $\mathrm{Zn}_{1-x}\mathrm{Ni}_x\mathrm{S}$, and $\mathrm{Zn}_{1-x}\mathrm{Cr}_x\mathrm{S}$, and indeed additional modes lying between the TO and LO lines have been observed[4] in these cases. It is surprising that the frozen-mode mode behavior persists to such high ($y \approx 0.5$) impurity concentrations and this raises some obvious questions. To answer some of these questions it would now be interesting to carry out similar investigations on a series of samples that are doped from both the *AB* end and the *AC* end. This would enable one to investigate a "crossover" regime and gain additional insight into the origin of such frozen-mode behavior. A review of the existing data suggests that the reduced mass difference criterion might also be appropriate for the prediction of single-mode ($2 \lesssim \Delta\mu \lesssim 7$ amu) and two-mode ($\Delta\mu \gtrsim 7$ amu) behavior. We may conclude, from the above-mentioned observations, that when the reduced mass difference of the end members is small ($\Delta\mu \lesssim 2$), the ternary crystals respond driven mainly by disorder effects caused by the random incorporation of the dopant species, that is, additional phonon modes are observed which relate to peaks in the one-phonon density of states and the frequencies of the TO and LO modes remain constant (frozen-mode behavior). If the reduced mass difference increases within certain limits ($2 \lesssim \Delta\mu \lesssim 7$ amu), the corresponding modes of the *AB* and *AC* sublattices are able to couple and yield only a pair of LO-TO modes (one-mode behavior). Finally, if the reduced mass difference increases further ($\Delta\mu \gtrsim 7$ amu), the phonons of the *AB* and *AC* sublattices decouple and two pairs of LO-TO modes are observed. It thus appears that the value of the reduced mass difference might serve as a simple, powerful criterion for the characterization of the optical modes in ternary mixed compounds. From the physical point of view, the $\Delta\mu$ criterion considers the crystal as formed by two sets of two-mass oscillators (one set formed with masses *A* and *B* and the other with masses *A* and *C*), and compares their reduced masses to elucidate the dynamic response of the mixed system.

A final remark related to the frozen-mode behavior and the criterion proposed by Chang and Mitra: according to Eq. (1), mixed crystals such as $\mathrm{Zn}_x\mathrm{Fe}_{1-x}\mathrm{S}$ and $\mathrm{Zn}_x\mathrm{Mn}_{1-x}\mathrm{S}$ should present one-mode behavior; however, a frozen-mode behavior is observed. This does not represent necessarily a complete failure of Chang and Mitra's model, since the frozen-mode behavior could be considered as a special case of the one-mode behavior in the sense that only a pair of TO-LO modes are present with the particularity that the frequencies of these phonon modes remain constant. That is, in a (frequency of TO an LO modes) vs (x, impurity percentage) graph, the lines describing the variation of the modes frequency would be nearly horizontal, within experimental error, as the behavior of the LO mode in Fig. 3. In this way, the criterion given for the frozen-mode behavior $\Delta\mu \lesssim 2$ could be thought as complementary to Eq. (1). It has been shown, however, that the consideration of the reduced mass differences does not find application only for frozen modes, for exists a direct relationship between the magnitude of $\Delta\mu$ and the one- and two-mode behaviors. The reason why the border line values for $\Delta\mu$, ~ 2 and ~ 7, obtained from the experimental data, are so is not clear at this point. Additional theoretical work is required to determine more precisely the border values in terms of physical parameters of the parent binary compounds.

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[1] For a review, see K. Furdyna and J. Kossut, *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, San Diego, 1988), Vol. 25.

[2] C. L. Mak, R. Sooryakumar, B. T. Jonker, and G. A. Prinz, Phys. Rev. B **45**, 3344 (1992).

[3] For a review, see I. F. Chang and S. S. Mitra, Adv. Phys. **20**, 359 (1971).

[4] M. Zigone, M. Vandevyver, and D. N. Talwar, Phys. Rev. B **24**, 5763 (1981).

[5] W. Hayes and R. Loudon, *Scattering of Light by Crystals* (John Wiley & Sons, New York, 1978).

[6] N. Vagelatos, D. Wehe, and J. S. King, J. Chem. Phys. **60**, 3613 (1974).

[7] L. A. Felkkamp, D. K. Steinman, N. Vagelatos, J. S. King, and G. Venkataraman, J. Phys. Chem. Solids **32**, 1573 (1971).

[8] J. Bergsma, Phys. Lett. **32A**, 324 (1970).

[9] K. Kunc, M. Balkanski, and M. A. Nusimovici, Phys. Rev. B **12**, 4346 (1975).

[10] O. Brafman and S. S. Mitra, Phys. Rev. **171**, 931 (1968).

[11] W. G. Nilsen, Phys. Rev. **182**, 838 (1969).

[12] J. C. Irwin, Can. J. Phys. **48**, 2477 (1970).

[13] A. V. Krol', N. V. Levichev, A. L. Natadze, and A. I. Ryskin, Fiz. Tverd. Tela (Leningrad) **20**, 154 (1978) [Sov. Phys. Solid State **20**, 85 (1978)].

[14] R. J. Nemanich and S. A. Solin, Phys. Rev. B **20**, 392 (1979).

[15] J. G. Naeini, B. M. Way, J. Dahn, and J. C. Irwin, Phys. Rev. B **54**, 144 (1996).

[16] W. Giriat and J. K. Furdyna, in *Semiconductors and Semimetals*, edited by J. K. Furdyna and J. Kossut (Academic, San Diego, 1988), Vol. 25, pp. 1–33.

[17] D. L. Peterson, A. Petrou, W. Giriat, A. K. Ramdas, and S. Rodríguez, Phys. Rev. B **33**, 1160 (1986).

[18] H. L. Park and W. B. White, Phys. Status Solidi B **144**, K69 (1987).

[19] S. Sourisseau, R. Cavagnat, and M. Fouassier, J. Phys. Chem. Solids **52**, 537 (1991).

[20] S. Ushioda, Solid State Commun. **10**, 307 (1972).

[21] C. de las Heras, I. J. Ferrer, and C. Sánchez, J. Phys.: Condens. Matter **6**, 1 (1994).

[22] A. L. Natadze, I. V. Pevnitskii, A. I. Ryskin, and G. I. Khil'ko, Fiz. Tverd. Tela (Leningrad) **18**, 1933 (1976) [Sov. Phys. Solid State **18**, 1125 (1976)].

[23] M. Zigone, R. Beserman, and M. Balkanski, in *Proceedings of the Second International Conference on Light Scattering in Solids*, edited by M. Balkanski (Flamarion Sciences, Paris, 1971), p. 61.

[24] S. A. López-Rivera, Jpn. J. Appl. Phys., Part 1 **32**, Suppl. 32-3, 403 (1993).

[25] K. Kunc and H. Bilz, Solid State Commun. **19**, 1027 (1976).

[26] O. Goede and W. Heimbrodt, Phys. Status Solidi B **146**, 11 (1988).

[27] E. Jahne, O. Goede, and V. Weinhold, Phys. Status Solidi B **146**, K157 (1988).

[28] L. Genzel, T. P. Martin, and C. H. Perry, Phys. Status Solidi B **62**, 83 (1974).

[29] E. Jahne, Phys. Status Solidi B **75**, 221 (1976).

[30] R. J. Elliot, J. A. Krumhansl, and P. L. Leath, Rev. Mod. Phys. **46**, 465 (1974).

[31] J. C. Irwin and J. LaCombe, Can. J. Phys. **50**, 2596 (1972).

[32] S. Venugopalan, A. Petrou, R. R. Galazka, A. K. Ramdas, and S. Rodríguez, Phys. Rev. B **25**, 2681 (1982).

[33] Shin-ichi Nakashima, Takaaki Fukumoto, Akiyoshi Mitsuishi, and Kohji Itoh, J. Phys. Soc. Jpn. **35**, 1437 (1973).

[34] Yu A. Mityagin, L. K. Vodopyanov, and E. A. Vinogradov, Fiz. Tverd. Tela (Liningrad) **17**, 2054 (1975) [Sov. Phys. Solid State **17**, 1341 (1976)].

[35] G. Lucovsky, A. Mooradian, W. Taylor, G. B. Wright, and R. C. Keezer, Solid State Commun. **5**, 113 (1967).

[36] M. P. Lisitsa, M. Ya. Valakh, and N. K. Konovets, Phys. Status Solidi **34**, 269 (1969).

[37] Shin-ichi Nakashima, Takaaki Fukumoto, and Akiyoshi Mitsuishi, J. Phys. Soc. Jpn. **30**, 1508 (1971).

[38] O. Brafman, Solid State Commun. **11**, 447 (1972).

[39] R. G. Alonso, E. K. Suh, A. K. Ramdas, N. Samarth, H. Luo, and J. K. Furdyna, Phys. Rev. B **40**, 3720 (1989).

[40] M. L. Gòrska and W. Nazarewicz, Phys. Status Solidi B **57**, K65 (1973).

[41] O. Brafman, I. F. Chang, G. Lengyel, S. S. Mitra, and E. Cranall, Jr., in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 602.

[42] D. N. Talwar, Z. C. Feng, and P. Becla, Phys. Rev. B **48**, 17 064 (1993).

[43] D. Huang, C. Jin, D. Wang, X. Liu, J. Wang, and X. Wang, Appl. Phys. Lett. **67**, 3611 (1995).

[44] A. Mooradian and T. C. Harman, *Physics of Semimetals and Narrow Gap Semiconductors*, edited by D. L. Carter and R. J. Bate (Pergamon, Oxford, 1971), p. 297.

[45] J. F. Parrish, C. H. Perry, O. Brafman, I. F. Chang, and S. S. Mitra, *II-VI Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), p. 1164.

[46] I. F. Chang and S. S. Mitra, Phys. Rev. **172**, 924 (1968).

[47] A. K. Garg, J. Phys. C **19**, 3949 (1986).

[48] R. Vogelgesang, A. J. Mayur, M. D. Sciacca, E. Oh, I. Miotkowski, A. K. Ramdas, S. Rodríguez, and G. Bauer, J. Raman Spectrosc. **27**, 239 (1996).

[49] R. Besserman, C. Hirliman, M. Balkanski, and J. Chevalier, Solid State Commun. **20**, 485 (1976).

[50] R. M. Abdelouhab, R. Braustein, K. Barner, M. A. Rao, and H. Kroemer, J. Appl. Phys. **66**, 787 (1989).

[51] B. Jusserand and S. Slemkes, Solid State Commun. **49**, 95 (1984).

[52] G. Lucovsky, R. D. Burnham, and A. S. Alimonda, Phys. Rev. B **14**, 2503 (1976).

[53] G. Armelles, J. M. Calleja, and E. Muñoz, Solid State Commun. **65**, 779 (1988).

[54] T. C. McGlinn, T. N. Krabach, M. V. Klein, G. Bajor, J. E. Greene, B. Kramer, S. A. Barnett, A. Lastras, and S. Gorbatkin, Phys. Rev. B **33**, 8396 (1986).

[55] R. M. Cohen, M. J. Cherng, R. E. Benner, and G. B. Stringfellow, J. Appl. Phys. **57**, 4817 (1985).

[56] S. Emura, S-I. Gonda, Y. Matsui, and H. Hayashi, Phys. Rev. B **38**, 3280 (1988).

[57] G. Lucovsky and M. F. Chen, Solid State Commun. **8**, 1397 (1970).

[58] H. Asahi, S. Emura, and S-I. Gonda, J. Appl. Phys. **65**, 5007 (1989).

[59] P. Galtier, J. Chevallier, M. Zigone, and G. Martínez, Phys. Rev. B **30**, 726 (1984).

[60] M. H. Brodsky, G. Lucovsky, M. F. Chen, and T. S. Plaskett, Phys. Rev. B **2**, 3303 (1970).

[61] B. Jusserand and J. Sapriel, Phys. Rev. B **24**, 7194 (1981).

[62] O. K. Kin and W. G. Spitzer, J. Appl. Phys. **50**, 4362 (1979).

[63] R. Carles, N. Saint-Cricq, J. B. Renucci, and R. J. Nicholas, J. Phys. C **13**, 899 (1980).

[64] D. N. Talwar, M. Vandevyver, and M. Zigone, J. Phys. C **13**, 3775 (1980).

[65] N. P. Kelkelidze, G. P. Kelkelidze, and Z. D. Makharadze, J. Phys. Chem. Solids **34**, 2117 (1973).

[66] G. Lucovsky, K. Y. Cheng, and G. L. Pearson, Phys. Rev. B **12**, 4135 (1975).

[67] Y. T. Cherng, D. H. Jaw, M. J. Jou, and G. B. Stringfellow, J. Appl. Phys. **65**, 3285 (1989).

[68] S. Emura, T. Nakayawa, and S-i Gonda, J. Appl. Phys. **62**, 4632 (1987).