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Local and gap modes of substitutional $3d$ transition-metal ions in zinc-blende and wurtzite II-VI semiconductors

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The localized vibrational modes of the $3d$ transition-metal ions (TMI's) substituting for the cations in CdTe, ZnTe, and CdSe appear in infrared absorption with as many lines as there are isotopes of the impurity and with intensities proportional to their natural abundances. The triply degenerate local mode in a zinc-blende host splits into a singlet and a doublet in a wurtzite host, the former appearing only when the electric vector ($\mathbf{E}$) of the incident radiation is parallel to the optic axis ($\hat{c}$) and the latter when $\mathbf{E}\perp\hat{c}$. Replacement of Cd by a TMI in CdSe results in high-frequency local vibrational as well as gap modes lying in the gap between the acoustic- and optic-phonon branches, the latter exhibiting an optical anisotropy similar to that of the former. Both the local and the gap modes exhibit a unique *nonmonotonic* trend across the $3d$ transition-metal series, with a minimum at Mn. [S0163-1829(96)09519-7]

I. INTRODUCTION

The wide range of physical properties of the tetrahedrally coordinated II-VI semiconductors significant in the context of basic physical issues[1] and semiconductor quantum well lasers in the blue green[2] have generated considerable current interest in their study. The successful growth of II-VI ternary and quaternary alloys over a large composition range, in turn, offers a flexible control over their semiconducting, optical, and structural properties such as band gaps, phonons, and lattice parameters. A unique subset of the II-VI alloys is the diluted magnetic semiconductor (DMS), in which some of the group II atoms are replaced with an element of the $3d$ transition-metal series; in addition to their semiconducting properties, such DMS's exhibit spectacular magnetic and magneto-optic phenomena.[1] The recent growth of DMS-based epilayers, multiple quantum wells, and superlattices have created further opportunities for both physical studies and novel applications.

The Mn-based II-VI's in which Mn replaces Zn, Cd, or Hg are the most extensively studied DMS's thanks to their high miscibility while maintaining the zinc-blende or wurtzite structure characteristic of the II-VI host. For example, $Cd_{1-x}Mn_xTe$ retains the zinc-blende structure of the CdTe host for x as high as 0.77 even though MnTe crystallizes in the distinctly different NiAs structure. Although the other elements of the $3d$ series have a similar outer shell configuration, i.e., $3d^n4s^2$, their incorporation is significantly smaller than that of Mn; it is tempting to speculate as to whether this behavior is associated with the exactly half-filled d shell of Mn. Nonequilibrium growth techniques, however, do enable the realization of a significantly larger incorporation of the $3d$ transition metals in the II-VI's; in fact, even zinc-blende MnTe and MnSe have been successfully grown, but only as epilayers and constituents of multiple quantum wells.[3] The insights gained from the investigations on Mn-based alloys are now being applied to the understanding of the electronic structure and vibrational properties of DMS's based on the other $3d$ transition-metal elements.

The vibrational spectra of the II-VI–based alloys and DMS's provide classic illustrations of the lattice dynamics of mixed crystals. The relative masses of the atoms constituting the alloy and the force constants characterizing the interatomic bonds determine the pattern of the evolution of the ''multimode behavior'' of the zone-center optical-phonon frequencies with composition.[4,5] The zone-center optical phonons of $Cd_{1-x}Mn_xTe$ display a ''two mode'' behavior[6] with distinct CdTe-like and MnTe-like LO-TO (where LO is longitudinal optic and TO is transverse optic) phonon pairs because of the significant mass difference between the cations Cd and Mn. Correspondingly, in the reflectivity spectra there are two distinct reststrahlen bands.[7] In contrast, the zone-center optical phonons of $Zn_{1-x}Mn_xTe$ exhibit a more complex behavior termed ''intermediate''[8] due to the closer match between the Zn and Mn masses. In a quaternary system with three different cations as in $Cd_{1-x-y}Mg_xMn_yTe$, the significantly different masses of the three cations leads to an unambiguous ''three mode'' behavior[9] with MgTe-like, MnTe-like, and CdTe-like LO-TO phonon pairs in decreasing order of frequency. However, the multimode behavior of a quaternary such as $Cd_{1-x-y}Zn_xMn_yTe$ is more complex,[10] again on account of the closer match between the Zn and Mn masses, with only the CdTe-like LO-TO pair remaining distinct with composition, the MnTe-like and ZnTe-like LO-TO pairs exhibiting an intermediate mode behavior. The multimode behavior of only the Mn-based DMS's has been investigated extensively with the exception of $Zn_{1-x}Fe_xSe$ and $Zn_{1-x}Co_xSe$.[11] The collective vibrations involving the zone-center phonons at high transition-metal ion (TMI) concentrations emerge from the localized vibration of the TMI when

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present in extreme dilution. Such an evolution of the local mode of substitutional Mg^{2+} in CdTe into the collective zone-center ''MgTe-like'' mode has indeed been investigated by Oh *et al.*[9] It is therefore of fundamental interest to study the localized vibrations of the TMI's in the II-VI's as a starting point towards an understanding of the vibrational properties of the DMS's.

The TMI's are all lighter than the cations (Zn, Cd, or Hg) as well as the anions (Se or Te). Thus the replacement of the cation by any of the TMI's leads to a localized vibrational mode (LVM) above the reststrahlen. At extreme dilution the isotopic nature of the substitutional TMI clearly manifests itself in the infrared spectrum of its LVM and provides a fingerprint for the impurity. Each triply degenerate, infrared active, LVM of a given impurity isotope in a zinc-blende host undergoes a splitting in a wurtzite host into two components, a nondegenerate mode polarized along the optic axis and a doubly degenerate mode normal to it. The characteristic fine structure in the LVM of the TMI's associated with the host-isotope disorder, revealed under ultrahigh resolution, has been addressed in the preceding paper. A unique trend in the LVM frequency as a function of the number of 3*d* electrons of the TMI provided an additional motivation for the present study.[12] In the present paper we report the results of a systematic investigation of the infrared spectrum of the LVM's and the gap modes of the TMI's in the zinc-blende CdTe and ZnTe as well as in the wurtzite CdSe.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The spectrometer and the associated equipment as well as the procedure for sample preparation are described in the preceding paper. The crystals were grown by the vertical Bridgman technique and possessed nominal TMI concentrations of 10^{18}–10^{20} cm^{-3}. The details of the growth will be described elsewhere.[13] It was found that the CdSe crystals, which were opaque in the infrared region of interest, showed remarkable improvement in transmission after a post treatment in Se vapor at ~800 °C for approximately 12 h. (The treatment presumably removes the free carriers associated with Se vacancies, which act as shallow donors.)

A. Zinc-blende hosts: CdTe and ZnTe

The LVM of a light impurity in a host crystal is most commonly modeled[14] as an anharmonic oscillator confined to a potential consistent with the site symmetry of the impurity. Both CdTe and ZnTe have the zinc-blende structure and hence the substitutional TMI has T_d site symmetry, the irreducible representations being labeled as in Koster *et al.*[15] Thus the LVM observed in their infrared spectra is a triply degenerate mode of Γ_5 symmetry belonging to the point group T_d. The infrared absorption spectrum of CdTe:Ti^{2+} is displayed in Fig. 1 in the range 180–280 cm^{-1}. Five sharp signatures labeled ω_{LVM} are observed around 225 cm^{-1}, between the reststrahlen and a multiphonon band of CdTe. The inset shows the spectrum after subtracting the underlying pure CdTe absorption. Titanium has five stable isotopes whose natural abundances[16] are listed in Table I; hence one expects five LVM's in its absorption spectrum with intensities proportional to the natural abundances of the isotopes of Ti. On integrating the areas under these excitation lines, the relative intensities indeed justify their assignment to the LVM's of the Ti isotopes. The LVM's of substitutional Cr^{2+} in CdTe have been similarly identified. However, the LVM's associated with the different Cr isotopes are not fully resolved and a curve fitting procedure was employed to determine their intensities and positions. In the case of CdTe:Fe^{2+}, only the fundamental and second harmonic of the LVM associated with the most abundant ^{56}Fe isotope (91.7%) was observed with sufficient intensity. The monoisotopic Sc, Mn, and Co exhibit only a single LVM with intensities that scale with the nominal concentrations. Vanadium has one stable ^{51}V isotope with a natural abundance of 99.75% and a ^{50}V isotope (0.25%) with a half-life of 6×10^{15} yr. The LVM associated with the former has been observed, its intensity scaling with the nominal concentration of substitutional V^{2+}. The LVM's associated with substitutional Ni^{2+} and Cu^{2+} could not be observed, presumably due to insufficient incorporation in the samples studied. The frequencies of the fundamental and second harmonic LVM's of the various TMI's in CdTe are listed in Table I.

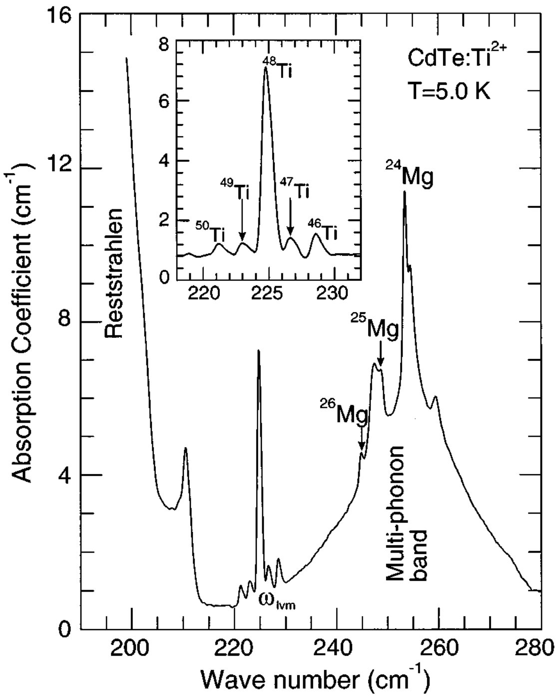

FIG. 1. The infrared absorption spectrum (at 0.5 cm^{-1} resolution) of CdTe:Ti^{2+} showing the five lines associated with the LVM's of the five Ti isotopes. The inset shows the spectrum after subtracting the underlying CdTe absorption. The lines labeled ^{24}Mg, ^{25}Mg, and ^{26}Mg are the LVM's associated with residual Mg in the sample.[18]

Similar experiments on ZnTe, another zinc-blende host doped with TMI's, have been performed and the observed LVM frequencies are listed in Table I. Again a curve fitting procedure was employed to establish the positions of the LVM's associated with the Cr isotopes; for substitutional Fe^{2+} only the LVM of ^{56}Fe was observed. The LVM associated with only the overwhelmingly abundant ^{51}V isotope was observed in its infrared spectrum, its intensity being proportional to the nominal concentration of substitutional V^{2+}. The concentration of substitutional Ti^{2+} was sufficient

TABLE I. Fundamental (ω_{LVM}) and second harmonic (ω_{SH}) frequencies (cm^{-1}) of the LVM's of substitutional TMI's in CdTe and ZnTe at $T=5.0$ K. The Mn impurity mode in ZnTe is resonant with the reststrahlen of ZnTe.

Transition metal	Mass number	Natural abundance[a] (%)	CdTe		ZnTe	
			ω_{LVM}	ω_{SH}	ω_{LVM}	ω_{SH}
Sc	45	100.0	245.1	489.3		
Ti	46	8.2	228.5			
	47	7.4	226.7			
	48	73.8	224.8		240.2	
	49	5.4	223.0			
	50	5.2	221.2			
V	51	99.75	210.2		223.9	
Cr	50	4.35	207.3		223.9	
	52	83.79	204.4		221.2	
	53	9.5	202.9		219.0	
	54	2.36	201.6		216.3	
Mn	55	100.0	191.2	381.3	resonant	
Fe	56	91.7	196.1	391.3	211.9	423.3
Co	59	100.0	199.0	397.5	217.5	

[a] Ref. 16.

for identifying the LVM associated with only the most abundant ^{48}Ti isotope. LVM's associated with Sc^{2+}, Ni^{2+}, and Cu^{2+} were not observed due to their low concentrations in the samples studied.

It is interesting to note that in spite of ^{50}Ti and ^{50}Cr having the same atomic mass, their LVM's in CdTe are distinct, viz., at 221.2 cm^{-1} and 207.3 cm^{-1}, respectively. In contrast, the LVM's of both ^{51}V and ^{50}Cr in ZnTe occur at 223.9 cm^{-1}, although they possess different atomic masses. It is immediately apparent from these examples that a simple mass defect model is inadequate, implying a change in the force constant brought about by the extent of the incompleteness of the 3*d* shell. A nonmonotonic trend is indeed observed in the LVM frequencies in CdTe with a minimum at Mn. Such a trend is also evident in ZnTe although one has to deduce the minimum at Mn, where the softening of the Mn-Te bond coupled with the close match of the Zn and Mn masses locates the Mn impurity mode at 210.3 cm^{-1} between the LO and TO frequencies of ZnTe, thus resulting in an intermediate mode behavior.[8] Hence a direct observation of the Mn impurity mode in ZnTe in an infrared measurement is not possible. The nonmonotonic dependence of the LVM frequency on the number of 3*d* electrons of the TMI is discussed later.

B. Wurtzite host: CdSe

CdSe crystallizes in the wurtzite structure and a TMI substituting for Cd has C_{3v} site symmetry. As a consequence, the Γ_5 first excited state of the LVM associated with a substitutional impurity in T_d site symmetry splits into a nondegenerate and a doubly degenerate mode of symmetries Γ_1 and Γ_3, respectively, of the point group C_{3v}, the symmetry of the ground state being Γ_1.[17] The selection rules for infrared active transitions are $\Gamma_1 \rightarrow \Gamma_1$ for $\mathbf{E}\parallel\hat{c}$ and $\Gamma_1 \rightarrow \Gamma_3$ for $\mathbf{E}\perp\hat{c}$, where $\mathbf{E}$ is the electric vector of the incident radiation and $\hat{c}$ the optic axis. Figure 2 shows the absorption spectrum of CdSe:Co^{2+} in the spectral region where one expects the LVM. The two lines labeled ω_{LVM} observed above the reststrahlen, at 226.4 cm^{-1} and 229.3 cm^{-1} for $\mathbf{E}\parallel\hat{c}$ and $\mathbf{E}\perp\hat{c}$, respectively, are attributed to the LVM's of substitutional Co^{2+} in CdSe. Given the selection rules for electric dipole allowed transitions, the positions of the LVM's determine the ordering in which Γ_3 lies above Γ_1, as illustrated in the inset. The observed LVM frequencies of the TMI's in CdSe are listed in Table II. They again display a trend similar to that observed in the zinc-blende hosts with an increase from Mn to Fe to Co. Whether there is a minimum of ω_{LVM} at Mn can only be confirmed after observing the LVM's of the TMI's to the left of Mn in the 3*d* series. We have not observed the LVM's associated with these TMI's, Ni, and Cu, because of insufficient concentrations in the samples studied.

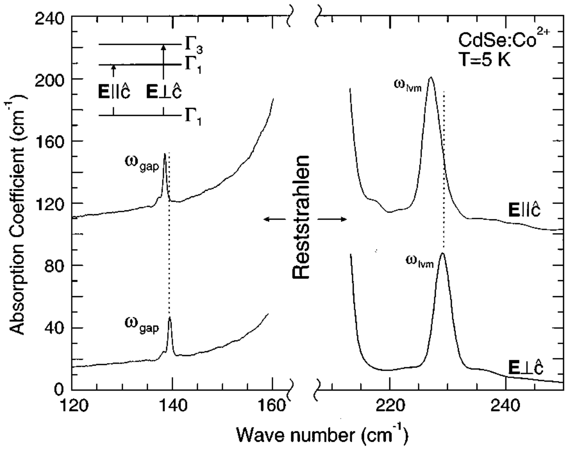

FIG. 2. The absorption spectra (at 0.5 cm^{-1} resolution) of CdSe:Co^{2+} for $\mathbf{E}\parallel\hat{c}$ (upper) and $\mathbf{E}\perp\hat{c}$ (lower) showing the anisotropy associated with the LVM of substitutional Co^{2+}. Gap modes showing a similar anisotropy are observed at frequencies below the reststrahlen. The vertical dotted lines are to guide the eye.

TABLE II. LVM and gap mode frequencies (cm^{-1}) of substitutional TMI's in CdSe for $\mathbf{E}\|\hat{c}$ and $\mathbf{E}\perp\hat{c}$ at $T=5.0$ K.

Transition metal	Mass number	LVM		Gap mode	
		$\mathbf{E}\|\hat{c}$	$\mathbf{E}\perp\hat{c}$	$\mathbf{E}\|\hat{c}$	$\mathbf{E}\perp\hat{c}$
Mn	55	220.0	222.0	137.6	138.7
Fe	56	222.0	224.8	138.2	138.5
Co	59	226.4	229.3	138.5	139.4

In both CdTe and ZnTe the anion is heavier than the cation, whereas in CdSe the cation is the heavier constituent. Substitution of the cation by a TMI in the former produces only a local mode above the reststrahlen of the host, whereas for a similar substitution in the latter, in addition to the high-frequency LVM, the existence of a vibrational ‘‘gap mode’’ with a frequency in the gap between the acoustic- and optic-phonon branches is predicted.[4] In Fig. 2 the two sharp lines labeled ω_{gap} at 138.5 cm^{-1} for $\mathbf{E}\|\hat{c}$ and at 139.4 cm^{-1} for $\mathbf{E}\perp\hat{c}$ below the reststrahlen of CdSe are attributed to the gap modes of substitutional Co^{2+} in CdSe. The observed gap mode frequencies of the substitutional TMI's in CdSe are also listed in Table II. The gap modes exhibit an optical anisotropy similar to that of the LVM's, with Γ_3 lying above Γ_1. The gap mode frequencies also follow the trend observed for the LVM frequencies, although the change is less pronounced for the gap mode as compared to that in the LVM.

C. LVM frequency and the electronic structure of the transition-metal ion

Inspection of the LVM frequencies in CdTe or ZnTe listed in Table I reveals an intriguing nonmonotonic trend across the 3*d* series with a minimum at the half-filled *d* shell of Mn^{2+}. For CdSe it is observed that the LVM frequencies in Table II increase from Mn to its right in the 3*d* series, although the minimum at Mn cannot be confirmed with the samples available. The trend is more transparent when one eliminates the mass dependence of the LVM frequency by defining an effective force constant $k=m\omega_{\mathrm{LVM}}^2$, where m is the atomic mass of the TMI. For the wurtzite host we define two effective force constants $k_\|$ and $k_\perp$ in a similar manner. (It should be noted that this estimate of the effective force constants neglects the motion of the NN Te or Se but is adequate for the present illustrative purposes.) In Fig. 3 we show a plot of k, $k_\|$, and $k_\perp$ as a function of the number of 3*d* electrons in the TMI based on the LVM frequency of its most abundant isotope; the singular chemical trend is immediately apparent. The intermediate mode behavior of $\mathrm{Zn}_{1-x}\mathrm{Mn}_x\mathrm{Te}$ does not permit a direct observation of the LVM of $^{55}\mathrm{Mn}$ in the infrared. However, in Fig. 3 the k for $\mathrm{ZnTe{:}Mn}^{2+}$ was deduced from the Raman line at 210.3 cm^{-1} for the Mn^{2+} impurity in ZnTe.[8] Figure 3 also shows the effective force constants for $^{40}\mathrm{Ca}$ in CdTe and ZnTe deduced in the manner described above from its LVM frequencies of 210.4 cm^{-1} and 228.5 cm^{-1}, in CdTe and ZnTe, respectively,[18] the significant distinction between Ca and the TMI's being the absence of 3*d* electrons in the outer shell of the former.

It is clear that the chemical trend reported here cannot arise from closed shell effects on bonding, which are known to vary monotonically across the rows of the Periodic Table. The role of the open 3*d* shell in the TMI's thus appears crucial for understanding the unique trend associated with their LVM's and consequently the nature of the bonding between the substitutional TMI and the host ligands. Following Zunger[19] one finds that the binding energy of an impurity atom to the host lattice is composed of both closed and open shell contributions. The open shell contributions, viz., the dominant multiplet correction energy, which represents a loss of binding energy in going from the localized *d*-state of the free ion to the more extended states in the solid, and the weaker crystal-field stabilization energy yield a net repulsive contribution to the TMI-anion binding energy. They further conspire in a manner such that the loss of binding energy is largest for Mn and decreases on either side of the 3*d* series (Fig. 15 of Ref. 19). One could in turn correlate the loss in binding energy with the weakening of the TMI-anion bonds and consequently the nonmonotonic trend observed in the LVM frequencies with a minimum at Mn.

III. CONCLUDING REMARKS

The present investigation has revealed that the LVM's of substitutional TMI's in CdTe, ZnTe, and CdSe exhibit a characteristic *isotope shift* associated with the different

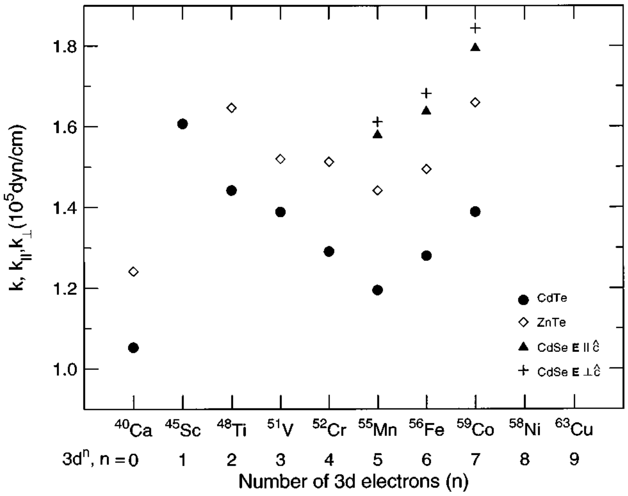

FIG. 3. Force constant dependence on the number of 3*d* electrons in the substitutional TMI in CdTe, ZnTe, and CdSe hosts. Also shown for comparison are the force constants for Ca^{2+} in CdTe and ZnTe.

nuclear masses of the isotopes of the TMI and an *optical anisotropy* when the host is a wurtzite, e.g., CdSe. Observation of the second harmonics ($\omega_{\rm SH}$) of the LVM's at slightly less than twice the fundamental ($\omega_{\rm LVM}$) frequency is indicative of anharmonic terms in the LVM potential, although the effect of anharmonicity as seen in ($2\omega_{\rm LVM}-\omega_{\rm SH}$) is less than 1% of $\omega_{\rm LVM}$. The rich fine structure present in the LVM's of the Ti isotopes in CdTe has not been observed in the LVM's of the other TMI's. The presence of a fine structure in the LVM's of Ti and Ca in the same CdTe sample, in which the LVM's of Mg and S were devoid of any, leads to the speculation that effects other than crystal quality have precluded the observation of the fine structure in the LVM's of the other TMI's. For ^{48}Ti in CdTe, the stretching (α) and bending (β) force constants of the XY_4 model deduced in the previous paper may be used to derive an effective force constant, $k=4(\alpha+4\beta)/3$ in the limit of infinitely massive NN's.[20] The value thus deduced, 1.15×10^5 dyn/cm, compares reasonably with 1.44×10^5 dyn/cm obtained using the simple ''mass on a spring'' model. Although the latter is an overestimate on account of ignoring the reduced mass of the oscillator, the nonmonotonic variation in the force constants with the minimum at Mn is still unmistakable. Indeed nonmonotonic trends in properties such as the crystal-field splitting energies, ground-state multiplet correction energies, and donor and acceptor ionization energies of substitutional TMI's in semiconductors have been reported and attributed to a hybridization of the localized d orbitals with the itinerant semiconductor bands.[19] The force constant variation described above could possibly be due to d-shell polarization effects or, more likely, crystal-field and multiplet splitting effects, which can affect the bonding through the sp-d hybridization. A weakening of the Mn-Te bond in $\rm Cd_{1-x}Mn_xTe$ has indeed been related to sp-d hybridization.[21] A quantitative evaluation of the local force constants from the observed LVM frequencies requires a complete description of the lattice dynamics of the host and a prediction of its variation with the number of $3d$ electrons appears to be possible only from a calculation of the electronic structure using d electron correlations. A study of the LVM's of the TMI's in the zinc-blende III-V semiconductors as well as in the II-IV-V$_2$ (e.g., ZnGeAs$_2$) and the I-III-VI$_2$ (e.g., AgGaSe$_2$) chalcopyrites is attractive in the context of the nonmonotonic trend discussed above. The electronic configuration of the TMI's substituting for the cations in the III-V's is $3d^{n-1}$, whereas in the chalcopyrites the inequivalent substitutional cation sites determines the electronic configuration. The nonmonotonic trend in the LVM frequencies may then display unusual effects such as a minimum at Fe, which now has the $3d^5$ configuration, in the III-V's. In the chalcopyrites, one expects two trends with minima at different points on the $3d$ series depending on the inequivalent substitutional sites.

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[1] See *Diluted Magnetic Semiconductors*, edited by J. K. Furdyna and J. Kossut, Semiconductors and Semimetals Vol. 25 (Academic Press, New York 1988).

[2] J. Ding, H. Jeon, A. V. Nurmikko, H. Luo, N. Samarth, and J. K. Furdyna, Appl. Phys. Lett. **57**, 2756 (1990); M. A. Haase, J. Qui, J. M. DePuydt, and H. Cheng, *ibid.* **59**, 1272 (1991); H. Jeon, J. Ding, W. Patterson, A. V. Nurmikko, W. Xie, D. C. Grillo, M. Kobayashi, and R. L. Gunshor, *ibid.* **59**, 3619 (1991).

[3] L. A. Kolodziejski, R. L. Gunshor, N. Otsuka, B. P. Gu, Y. Hefetz, and A. V. Nurmikko, Appl. Phys. Lett. **48**, 1482 (1986); J. Han, S. M. Durbin, R. L. Gunshor, M. Kobayashi, D. R. Menke, N. Pelekanos, M. Hagerott, A. V. Nurmikko, Y. Nakamura, and N. Otsuka, J. Cryst. Growth **111**, 767 (1991).

[4] A. S. Barker, Jr. and A. J. Sievers, Rev. Mod. Phys. **47**, S1 (1975).

[5] E. Oh and A. K. Ramdas, J. Electron. Mater. **23**, 307 (1994).

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

[7] W. Gebicki and W. Nazarewicz, Phys. Status Solidi B **86**, K135 (1978).

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

[9] E. Oh, C. Parks, I. Miotkowski, M. D. Sciacca, A. J. Mayur, and A. K. Ramdas, Phys. Rev. B **48**, 15 040 (1993).

[10] E. Oh, R. G. Alonso, I. Miotkowski, and A. K. Ramdas, Phys. Rev. B **45**, 10 934 (1992).

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

[12] Preliminary results of the local modes of the transition metals in CdTe, ZnTe, and CdSe are reported in A. J. Mayur, M. D. Sciacca, I. Miotkowski, G. C. La Rocca, A. K. Ramdas, and S. Rodriguez, Solid State Commun. **91**, 785 (1994).

[13] I. Miotkowski (unpublished).

[14] R. J. Elliot, W. Hayes, G. D. Jones, H. F. MacDonald, and C. T. Sennett, Proc. R. Soc. London Ser. A **289**, 1 (1965).

[15] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, MA, 1966).

[16] J. Emsley, *The Elements* (Oxford University Press, Oxford, England, 1993).

[17] R. C. Newman, *Infrared Studies of Crystal Defects* (Taylor and Francis, New York, 1973).

[18] M. D. Sciacca, A. J. Mayur, N. Shin, I. Miotkowski, A. K. Ramdas, and S. Rodriguez, Phys. Rev. B **51**, 6971 (1994).

[19] A. Zunger, *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic Press, New York, 1986), Vol. 39, p. 275.

[20] G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Princeton, NJ, 1960), p. 182.

[21] P. Maheshwaranathan, R. J. Sladek, and U. Debska, Phys. Rev. B **31**, 5212 (1985); S. B. Qadri, E. F. Skelton, A. W. Webb, E. R. Carpenter Jr., M. W. Schaefer, and J. K. Furdyna, *ibid.* **35**, 6868 (1987).