PHYSICAL REVIEW B VOLUME 41, NUMBER 9 15 MARCH 1990-II

Lattice dynamics of $AgGaSe_2$. II. Theoretical aspects

L. Artus
Institut de Ciència de Materials de Barcelona (ICMAB), Consell Superior d'Investigacions Cientifiques (CSIC), calle Marti i Franquès, E-08028 Barcelona, Spain

J. Pujol
Departament d'Engiyeria Mecànica, Escola Tecnica Superior d'Enginyers Industrials, E-08222 Terrassa, Spain

J. Pascual
Departament Fisica i Institut de Ciència de Materials de Barcelona (ICMAB), Consell Superior d'Investigacions Cientifiques (CSIC), Universitat Autònoma de Barcelona, E-08193 Bellaterra, Spain

J. Camassel
Groupe d'Etude des Semiconducteurs, Universitè des Sciences et Techniques du Languedoc, 34095 Montpellier CEDEX, France

(Received 16 August 1989)

We present a model calculation of the phonon spectrum of $AgGaSe_2$ which is the ternary analog of the pseudobinary II-VI-compound $Zn_{0.5}Cd_{0.5}Se$. We have used a simple Keating model and start from the series of force constants obtained by fitting independently the Raman modes of CdSe and ZnSe. Analyzing in great detail the dependence of the phonon frequencies and eigenvectors upon the different parameters which take part in the chalcopyrite distortion, we have successively taken into account the mass differences, the changes in force constants, the tetragonal distortion, and, finally, the anionic displacement. We have found a progressive constitution of the phonon spectrum in three bands with mainly ZnSe (GaSe) -like, CdSe (AgSe) -like, and mixed $CdZnSe_2$ ($AgGaSe_2$) -like characters. This accounts satisfactorily for most experimental data. To get even better agreement, we have performed a least-mean-squares fit of the four parameters which enter the calculation. We find, in this way, that the bond-stretching constant for Ga—Se bonds is about 50% higher than the one for Zn—Se bonds while, in contrast, the strengths of Ag—Se and Cd—Se bonds appear very similar. This improved series of parameters results in zone-center modes in very good agreement with the experimental values.

I. INTRODUCTION

In recent years, considerable interest has been devoted to the family of ternary compounds with the chalcopyrite structure. By substituting two cations (instead of simply one) in a regular ZnS-type lattice, one gets alternate series of bonds which results in structural as well as electronic anomalies. This point is now well understood[1] and, on the practical side, there is much interest in this class of materials, because of their potential applications in solar energy conversion and nonlinear optical devices, among others.

On the fundamental side, however, not much work deals with the phonon spectrum of chalcopyrite (and pnictide) materials. The simplest theoretical approach is to define a binary analog to each ternary ABC_2 compound by taking the (virtual) cation which is situated in the Periodic Table between the A and B atoms. In this case, the chalcopyrite (or pnictide) structures are nothing but superstructures of the ZnS-type lattice and, in the first order, one gets all zone-center modes by folding back (in a proper way) the dispersion branches of the ZnS-type (virtual) material.

In the preceding work,[2] hereafter referred to as paper I, we reported an experimental investigation of the lattice dynamics of $AgGaSe_2$. Performing infrared studies in the spectral range 15–500 cm^{-1} both at liquid-helium and room temperature, we could identify all Γ_4 ($\mathbf{E}\|c$) and Γ_5 ($\mathbf{E}\perp c$) vibrational modes predicted by group-theory arguments. This included (i) at low energy, folded-acoustic components resolved for the first time and (ii) at higher energy, a nearly degenerate Γ_5 doublet at 249.5–252.1 cm^{-1}. The frequencies obtained in this way were independently checked by performing, under nearly resonant conditions, Raman investigations at 77 K. In that way, we could then identify four additional modes: $1\Gamma_1$ and $3\Gamma_3$. Our experimental results demonstrated that all zone-center modes were grouped in three energy bands. First, within a very narrow energy range around 250 cm^{-1}, were four modes: $1\Gamma_3+1\Gamma_4+2\Gamma_5$; next, in an intermediate region extending from 180 to 135 cm^{-1}, were five modes which spanned a much wider range: $1\Gamma_1+1\Gamma_3+1\Gamma_4+2\Gamma_5$; and, finally, at much lower energy the dispersion of the acoustic branches gave in the range 25–85 cm^{-1} another series of four modes which are associated with $1\Gamma_3+1\Gamma_4+2\Gamma_5$ symmetry.

The standard assignment, in terms of Γ, X, and W phonon modes of the analogous $Zn_{0.5}Cd_{0.5}Se$ material, correctly predicts three vibrational bands. However, within a band, it fails to give the right number of components and, from band to band, cannot account for the range of experimental dispersion (see Table III of Paper I). This is because it completely overlooks the peculiarities of $AgGaSe_2$ and assumes that both "Ag-Se" and "Ga-Se" interactions are not significantly different. As a matter of fact, the interatomic distances in $AgGaSe_2$ (Ref. 3) are $d(\text{Ga-Se})=2.39$ Å and $d(\text{Ag-Se})=2.66$ Å. They are very close to their II-VI counterparts:[4] $d(\text{Zn-Se})=2.45$ Å and $d(\text{Cd-Se})=2.63$ Å, and show that $AgGaSe_2$ is not an averaged material. It is an original (truly intermediate) admixture of ZnSe and CdSe bonds. In the first case, the phonon energy spectrum spans[5,6] between 253 cm^{-1} for the Γ_{15}(LO) mode and 70 cm^{-1} for the X_5(TA) mode. In the second case, we have, of course, no available information concerning the cubic material but we can compare with the wurtzite form. In the literature, all frequencies range[7,8] between 193 cm^{-1}, for the LO component of the high-energy mode, and 34 cm^{-1}, for the lowest-frequency one. Since the range of experimental values found in Paper I (from 26 to 277 cm^{-1}) really spans the entire spectrum of ZnSe and CdSe modes, it is interesting to know how much of the atomic-like character is conserved within a given vibrational band.

In this work, we investigate the lattice dynamics of $AgGaSe_2$ from this simple viewpoint. We start from the well-known results of Ref. 9 and use a simple Keating model with only two series of parameters. One corresponds with central bond-stretching constants (α) which connect two first-nearest neighbors, the second corresponds with noncentral bond-bending constants (β) and is associated with three-body angular interactions. In this case, one neglects to discriminate between the different configurations *CAC* (cation-anion-cation) and *ACA*. As a matter of fact, this simple model gives a surprisingly good fit in the zinc-blende materials[10] (even if the localization implied by the intuitively appealing picture of bond bending is severely questioned) and seems most useful to set up a clear basis for discussion.

A most common difficulty with such simple models is to account for the flattening of the transversre acoustic branches. In a previous work, Bettini[11] used the same approach and attempted only to account for phonon modes which originate from the optical and longitudinal acoustic branches. In this work, all modes have been considered with reasonable success.

In the first section, we start from the folded-zone scheme and analyze the discrepancies which appear with respect to the experimental data. In the next part, we check how much of the phonon spectrum of $AgGaSe_2$ can be associated to Ag—Se bonds ("ZnSe"-like modes) and Ga—Se bonds ("CdSe"-like modes). This is done by inspection of the virtual compound $CdZnSe_2$ assigned to the same chalcopyrite structure. Lastly, in the third part, we determine the set of force constant parameters for $AgGaSe_2$ which best fit the experimental data.

II. $(Cd_{0.5}Zn_{0.5})Se$ AND THE FOLDED-ZONE SCHEME

Let us start from the results of Paper I. Since we based our discussion of the lattice dynamics of $AgGaSe_2$ (as obtained from the collection of infrared and Raman spectra) on the folded-zone scheme, we shall first investigate, as the simplest quantitative approach, the dispersion of the standard pseudobinary analog:[1] $(Cd_{0.5}Zn_{0.5})Se$. We shall assume an undistorted zine-blende structure, with a single (virtual) cation species and shall call it $Cd_{0.5}Zn_{0.5}$. We shall then define the corresponding series of parameters by averaging first the Cd and Zn atomic masses and

TABLE I. Phonon energies of ZnSe and "cubic" CdSe zinc-blende compounds at points Γ, X, and W. These points fold into Γ in the chalcopyrite structure. α (bond stretching) and β (bond bending) are the two force constant parameters which, entering the Keating model, determine the phonon energies. They are given in units of 10^3 erg cm^{-2}.

	ZnSe			CdSe	
Mode	Energy (cm^{-1})		Mode	Energy (cm^{-1})	
	Theory[a]	Experiment[b]		Theory[a]	Experiment[c]
Γ_{15}	238	207	Γ_{15}	166	166
W_2	217	214	W_2	161	
W_4	215	213	W_2	161	
X_5	211	206	X_5	160	
X_1	181	223	X_3	128	
W_1	170	150	W_3	126	
X_3	165	190	X_1	108	
W_3	155	201	W_1	105	
W_4	95	115	W_2	38	
W_2	94	93	W_4	38	
X_5	85	70	X_5	34	34
α	24.53		17.63		
β	3.88		0.82		

[a] This work.
[b] Reference 6.
[c] Reference 8 (wurtzite form).

second all "CdSe"-like and "ZnSe"-like force constants.

To get realistic values for these parameters in the binary materials, we have made preliminary calculations. Concerning ZnSe, a least-mean-squares fit to the experimental Raman frequencies[6] at points Γ, X, and W of the Brillouin zone (BZ) has been done. We have listed the series of force constants and phonon energies in Table I. Performing, next, a comparison with the neutron diffraction data of Ref. 5, we have found the results displayed in Fig. 1. Obviously, this supports our simple model. Finally, concerning the force constants obtained in this work, we notice a reasonable agreement with the different values reported by Kane[10] for similar materials.

Concerning CdSe, we had only poor experimental information and both Keating parameters were obtained from a very crude approximation. Starting from data obtained on the wurtzite form, we noticed that the extreme Raman frequencies were observed[8] at 166 and 34 cm^{-1}. Assuming that these values can be approximately identified with the Γ_{15} (TO) and X_5(TA) modes of a standard ZnS-type material, we get the series of force constants, and theoretical estimates of the phonon energies in cubic CdSe, which have been listed in Table I.

Taking now an average of the force constants (and atomic masses) of ZnSe and CdSe to constitute the virtual cation $Zn_{0.5}Cd_{0.5}$, we obtain the phonon energies at Γ, X, and W points in $Zn_{0.5}Cd_{0.5}Se$, which have been listed in Table II. Clearly, they do not really compare with the experimental data and only a rough, qualitative, agreement can be found. The most interesting conclusions concern the ordering of modes and the corresponding cationic contributions. As already discussed, three bands accommodate the 15 optic modes of the chalcopyrite structure. First six modes appear in the high-frequency range (180–200 cm^{-1}). They come directly from the splitting of the Γ_{15} cubic frequency and the folding of the TO branches with zone-boundary symmetry: $X_5+2W_2+2W_4$. Because of the complex compatibility

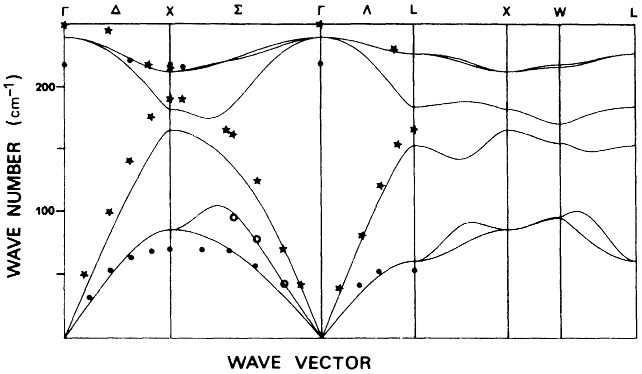

FIG. 1. Comparison of the phonon dispersion curves computed in this work for ZnSe (solid lines) with the neutron diffraction data of Ref. 5. In the computation, only two force constants have been used and correspond to the simple Keating model (Ref. 9). They have been independently adjusted by performing a least-mean-squares fit to the Raman data of Ref. 6.

TABLE II. Comparison of the optical frequencies of $AgGaSe_2$ with the theoretical calculations. The different approaches correspond to (a) folding the virtual compound $Cd_{0.5}Zn_{0.5}Se$; (b) considering the fictitious chalcopyrite compound $CdZnSe_2$; (c) performing least-mean-squares fit to experimental results of the first column, with (I) three or (II) four parameters. α_1 (α_2) and β_1 (β_2) are the force constants between anions and light (heavy) cations. All are in units of 10^3 erg/cm^2.

$AgGaSe_2$ (Ref. 2)		(a) $(Cd_{0.5}Zn_{0.5})_2Se_2$		(b) $CdZnSe_2$		(c) $AgGaSe_2$ (I)		(c) $AgGaSe_2$ (II)	
Mode	(cm^{-1})	Mode	(cm^{-1})	Mode	(cm^{-1})	Mode	(cm^{-1})	Mode	(cm^{-1})
Γ_{5T}	255	$\Gamma_5(\Gamma_{15})$	199	$\Gamma_5(\Gamma_{15})$	227	Γ_5	269	Γ_5	270
Γ_3	253	$\Gamma_4(\Gamma_{15})$	199	$\Gamma_4(\Gamma_{15})$	219	Γ_4	261	Γ_4	260
Γ_{4T}	252	$\Gamma_3(W_2)$	185	$\Gamma_5(W_4)$	206	Γ_5	243	Γ_5	243
Γ_{5T}	251	$\Gamma_4(W_2)$	185	$\Gamma_3(W_2)$	196	Γ_3	231	Γ_3	230
		$\Gamma_5(W_4)$	184						
		$\Gamma_5(X_5)$	182	$\Gamma_5(X_5)$	162	Γ_2	186	Γ_2	179
				$\Gamma_4(W_2)$	162	Γ_5	170	Γ_5	167
Γ_1	181	$\Gamma_2(X_1)$	147	$\Gamma_2(X_1)$	151	Γ_4	166	Γ_4	166
Γ_{5T}	162	$\Gamma_2(W_1)$	141	$\Gamma_1(W_1)$	144	Γ_1	162	Γ_1	162
Γ_3	160	$\Gamma_1(W_1)$	141	$\Gamma_3(X_3)$	135	Γ_5	140	Γ_3	143
Γ_{4T}	155	$\Gamma_3(X_3)$	139	$\Gamma_2(W_1)$	133	Γ_3	133	Γ_2	139
Γ_{5T}	137	$\Gamma_5(W_3)$	133	$\Gamma_5(W_3)$	132	Γ_2	131	Γ_5	138
Γ_{5T}	84	$\Gamma_5(W_4)$	69	$\Gamma_5(W_4)$	78	Γ_5	62	Γ_5	84
Γ_{4T}	58	$\Gamma_4(W_2)$	68	$\Gamma_4(W_2)$	65	Γ_4	59	Γ_4	60
Γ_3	58	$\Gamma_3(W_2)$	68	$\Gamma_3(W_2)$	61	Γ_3	58	Γ_3	51
Γ_{5T}	27	$\Gamma_5(X_5)$	61	$\Gamma_5(X_5)$	49	Γ_5	53	Γ_5	27
α_1			21.08		24.53		36.93		34.82
α_2			21.08		17.63		18.87		18.65
β_1			2.35		3.88		0.80		2.56
β_2			2.35		0.82		0.80		−0.54

relations already discussed in Paper I, this results in $1\Gamma_3+2\Gamma_4+3\Gamma_5$ modes in the chalcopyrite structure. Five modes appear next and constitute the second band. They come from the folding of the LO and LA branches with symmetry $X_1+2W_1+X_3+2W_3$ and give, in the chalcopyrite structure, $1\Gamma_1+2\Gamma_2+1\Gamma_3+1\Gamma_5$. We find, again, a very narrow range from 130 to 150 cm^{-1}. Finally, four modes appear in the low-frequency range. They constitute also a very narrow band (60–70 cm^{-1}) and come from the folding of the TA branches with symmetry $X_5+2W_2+2W_4$. This gives $1\Gamma_3+1\Gamma_4+1\Gamma_5$.

As already said, this general trend accounts (qualitatively) for the three bands of infrared and Raman frequencies observed in Paper I but not for the details of the repartition. The upper band is predicted too low in energy and spreads along a too wide energy range. On the contrary, the intermediate and lower bands are much too narrow. Moreover the calculation predicts six (three) active frequencies in the high- (intermediate-) energy range, while the experimental results give four (five). The point is that, from the folded-zone scheme, the $2\Gamma_4$ mode is expected in the upper energy band, while only one is found. Similarly, three Γ_5 frequencies are expected, while only two are found. This is a very important point to outline: in order to use the folded-zone scheme as a quantitative basis for discussion, one must be sure to have two (three) Γ_4 (Γ_5) modes in the high-energy band. This is the easiest way to check for the magnitude of the crystal-field splitting between the two components Γ_3 and Γ_4 issued from the W_2 frequencies.

As a matter of fact, in AgGaSe_2, the experimental results indicate a Γ_3-Γ_4 crystal-field splitting of ~ 90 cm^{-1} and one (two) Γ_4 (Γ_5) modes appear in the intermediate-frequency range. This is why the folded-zone scheme cannot reasonably account for the essential features encountered in this material. From the lattice dynamics viewpoint, this is simply because the high-energy manifold (directly issued from the folding of the TO branches in this simple model) exhibits an unrealistic, equally weighted, participation of Cd and Zn atoms. This argument also explains the narrow width of the vibrational bands. The averaged cation mass (88.9 amu) being close to the anion mass (79.0 amu), a large Γ_{15}-X_5(TO) dispersion and a small X_1-X_3 splitting should be expected. This, together with the low X-W dispersion along the surface of the Brillouin zone, results in the wrong theoretical predictions made for the distribution of the 15 optical frequencies.

III. THE FICTITIOUS COMPOUND CdZnSe_2

A more realistic approach to AgGaSe_2 is to consider the fictitious compound CdZnSe_2. In this case, half the virutal cations $\text{Cd}_{0.5}\text{Zn}_{0.5}$ have been replaced by real cadmium atoms and the other half by zinc. Accordingly, the simplest Keating model must contain four force constants. They have been already obtained for the binary materials and listed in Table I. Remember that the bond-stretching constants correspond with pure Zn-Se and Cd-Se first-nearest-neighbor interactions, respectively, while the bond-bending constants refer similarly to Zn-Se-Zn and Se-Zn-Se or Cd-Se-Cd and Se-Cd-Se angular distortions. For the mixed Cd-Se-Zn angular tilts, we have used a simple averaged parameter.

Provided the specific geometry is known, we can now discuss (without the use of any additional parameter) how the presence of both cation species influences the zone-center modes of AgGaSe_2. In order to get a clear idea of the respective effects of masses, force constants, and structural distortions upon the ordering of modes in CdZnSe_2, we have computed phonon energies in the following sequence: (i) From the virtual $(\text{Cd}_{0.5}\text{Zn}_{0.5})_2\text{Se}_2$ compound to the ideal, undistorted, CdZnSe_2 chalcopyrite through changes in the cation masses and changes in the force constants, independently, and (ii) including the geometric (tetragonal and anionic) distortions to get closer to the real AgGaSe_2 structure.

A. Changes in cationic masses

The change in zone-center frequencies, when passing from $(\text{Cd}_{0.5}\text{Zn}_{0.5})_2\text{Se}_2$ to CdZnSe_2 through changes in cation masses, is shown in Fig. 2(a). The most important trends, which agree with the distribution of optical phonons in AgGaSe_2, can be summarized as follows.

(i) In much better agreement with the experimental data, four modes belong now to the high-energy band. This is because the system evolves from a mean (virtual) cation model, where both Cd and Zn participated with the same weight in the phonon spectrum, to a situation in which the high-energy modes become more ZnSe-like. On the contrary, the low-frequency modes are now associated with more CdSe-like character. This is only an effect of the reduced mass which participates in a given vibration and is best seen when considering the eigenstates associated to the different modes. For convenience, they have been listed in Table III. While four modes harden: $\Gamma_5[\Gamma_{15}]$; $\Gamma_4[\Gamma_{15}]$; $\Gamma_5[W_4]$; and $\Gamma_3[W_2]$; two modes soften: $\Gamma_5[X_5]$ and $\Gamma_4[W_2]$. As a consequence, two different series of crystal-field splitting appear. One is between both W_2-like modes, and comes because one partner moves up while the other one moves down. The computed value in this case is about 35 cm^{-1}. The second is between both Γ_{15}-like components. In this case, the two partner modes (Γ_4 and Γ_5) move up and have already taken a pure ZnSe-like character. We compute a much lower value: 8 cm^{-1}.

(ii) All vibrational modes already present in the intermediate range seem quite insensitive to the changes in cationic masses. This is what one should expect for the three modes: $\Gamma_2[X_1]$ $\Gamma_1[W_1]$, and $\Gamma_2[W_1]$ which, from symmetry considerations, correspond to pure anionic vibrations in the chalcopyrite structure. This is not the case for the modes $\Gamma_3[X_3]$ and $\Gamma_5[2W_3]$ and occurs only because they are associated to cationic vibrations with equal participation of both species (see Table III). In this case, neglecting the inequivalence of force constants for the two different interactions, the results of the computation depend only on the change in the reduced mass: 44 amu in $(\text{Cd}_{0.5}\text{Zn}_{0.5})_2\text{Se}_2$ to be compared with 42 amu in CdZnSe_2.

(iii) Finally, the change in cationic masses spreads the dispersion of the six low-energy modes. This is a weak

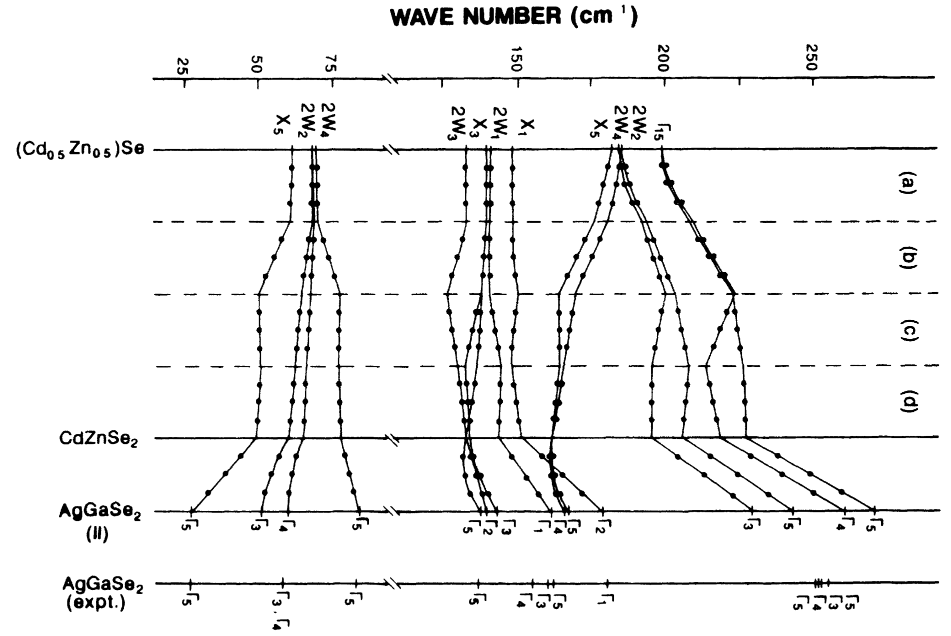

FIG. 2. Comparison of theoretical phonon energies, computed in this work, with experimental values for $AgGaSe_2$ (see Paper I). In this figure (a)–(d) display the evolution of optical modes, starting from the folded ZnS-like material $(Cd_{0.5}Zn_{0.5})Se$ up to the fictitious chalcopyrite compound $CdZnSe_2$: (a) is when changing the cation masses from $(m_{Cd}+m_{Zn})/2$ to m_C (where C=Cd,Zn); (b) is including the changes in force constants from mean (averaged) values to real CdSe- and ZnSe-like ones; (c) is adding the effects of the tetragonal distortion; and finally (d) is including the anionic displacement. Also shown are best fitted values (model $AgGaSe_2$ II) obtained with four disposable parameters (see text). Through the whole figure, all modifications have been computed assuming finite variations by steps of 25% of the final value. This shows the corresponding linear or nonlinear dependence of a given phonon branch.

effect and more interesting changes appear on the eigenstates. The highest degenerate mode ($\Gamma_5[W_4]$) hardens, and corresponds now to more ZnSe-like vibrations, while the low-energy vibration ($\Gamma_5[X_5]$) shifts down a few percent and takes more CdSe-like character. Again, the change of masses does not affect two modes, $\Gamma_3[W_2]$ and $\Gamma_4[W_2]$, which keep a mixed $(Cd_{0.5}Zn_{0.5})$ character.

B. Changes in force constants

Figure 2(b) displays the evolution of zone-center modes observed when using realistic Cd-Se and Zn-Se force con-

TABLE III. Normalized contribution of atomic displacements to the eigenstates of the various phonons. The different cases have been discussed in the text.

	$(Cd_{0.5}Zn_{0.5})_2Se_2$		$CdZnSe_2$			$AgGaSe_2$					
							(I)			(II)	
	Cd/Zn	Se	Cd	Zn	Se	Ag	Ga	Se	Ag	Ga	Se
$\Gamma_5(\Gamma_{15})$	0.44	0.56	0.00	0.62	0.38	0.00	0.58	0.42	0.00	0.62	0.38
$\Gamma_4(\Gamma_{15})$	0.44	0.56	0.00	0.58	0.42	0.00	0.54	0.46	0.00	0.56	0.44
$\Gamma_5(W_4)$	0.46	0.54	0.02	0.62	0.36	0.02	0.62	0.36	0.01	0.65	0.34
$\Gamma_3(W_2)$	0.40	0.60	0.02	0.58	0.40	0.01	0.59	0.40	0.01	0.63	0.36
$\Gamma_5(X_5)$	0.44	0.56	0.35	0.03	0.62	0.39	0.01	0.60	0.35	0.01	0.64
$\Gamma_4(W_2)$	0.40	0.60	0.24	0.00	0.76	0.30	0.00	0.70	0.23	0.01	0.76
$\Gamma_2(X_1)$	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00
$\Gamma_1(W_1)$	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00
$\Gamma_3(X_3)$	1.00	0.00	0.26	0.46	0.28	0.42	0.34	0.24	0.25	0.39	0.36
$\Gamma_2(W_1)$	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00
$\Gamma_5(W_3)$	1.00	0.00	0.42	0.40	0.18	0.52	0.30	0.18	0.43	0.33	0.24
$\Gamma_5(W_4)$	0.48	0.52	0.10	0.36	0.54	0.07	0.39	0.54	0.14	0.34	0.52
$\Gamma_4(W_2)$	0.54	0.46	0.26	0.34	0.40	0.24	0.34	0.42	0.31	0.31	0.38
$\Gamma_3(W_2)$	0.54	0.46	0.52	0.14	0.34	0.39	0.21	0.40	0.58	0.10	0.32
$\Gamma_5(X_5)$	0.50	0.50	0.42	0.06	0.52	0.39	0.09	0.52	0.44	0.06	0.50

stants in the ideal $CdZnSe_2$ chalcopyrite lattice. Since the force constants are stronger for Zn—Se bonds (in which participate the lighter cation) the overall effect is an enhancement of the trends already observed when changing the cationic masses. The four high-energy components harden appreciably (keeping a still better ZnSe-like character) and come closer to the experimental values. See Table II and III. On the contrary, the intermediate energy modes $\Gamma_4[W_2]$ and $\Gamma_5[X_5]$ correspond now to almost pure CdSe-like vibrations. Moreover, appearing at energy values very close to the one expected for the triply degenerate Γ_{15} mode in "cubic" CdSe (see Tables I and II), we believe that they should be more conveniently associated to Γ_{15}[CdSe]. This disagrees with the folding scheme but contains more physics.

Because the overall shift of these modes, starting from the folded positions W_2 and X_5, is very strong, they have mixed in the intermediate region with a series of frequencies issued from both LO and LA branches. However, not all participate in the "CdSe"-like manifold. This is because the old intermediate modes are quite insensitive to the size of the force constants and cannot be associated with any of the two different interactions. The only noticeable effect, in this case, is a progressive increase of the anionic character in both $\Gamma_3[X_3]$ and $\Gamma_5[W_3]$. However, one can easily check that both remain built from averaged cationic vibrations. This was already found in $(Cd_{0.5}Zn_{0.5})_2Se_2$ (see Table III). Finally, the effect induced upon the low-energy modes is similar to the one reported in the high-energy range. Because of the hardening of the "ZnSe"-like mode ($\Gamma_5[W_4]$) and the softening of the "CdSe"-like one ($\Gamma_5[X_5]$), respectively, they spread more in energy. This is in better agreement with the experimental data.

C. Structural distortions

Up until now we have only taken into consideration the replacement of a virtual type-II cation ($Cd_{0.5}Zn_{0.5}$) by real Cd and Zn atoms ordered in a regular ZnS-type lattice (ideal chalcopyrite structure). We considered the changes in cationic masses and cation-anion force constants but all anions were kept at the center of ideal undistorted tetrahedra. This does not correspond with the real situation: two structural distortions exist in real chalcopyrites, with respect to the ideal structure, and both must be taken into consideration.[1,12] One is the tetragonal compression; the second is the anionic displacement.

Of course, we have no experimental information concerning the structural distortions in the fictitious compound $CdZnSe_2$ but we know that all effects originate from the difference in bond lengths.[1] The force constants used in the preceding section, for Cd—Se and Zn—Se bonds, were calculated from real ZnSe and CdSe crystals where the bond lengths are within 2% of that of Ag—Se and Ga—Se in real $AgGaSe_2$. They give reasonable results and we believe that they should trigger similar structural distortions. In the case of $AgGaSe_2$, the tetragonal distortion parameter is $c/a = 1.793$, which represents a 10% deviation from the undistorted lattice. Similarly, the anionic displacement parameter is $u = 0.27$ (instead of 0.25 in the ZnS-type lattice) and, again, the deviation (8%) is rather large. Since both contributions result in changes of the geometrical factors, they will result in changes of the dynamical matrix.

Our computational results for the tetragonal compression and the anionic displacement have been shown separately in Figs. 2(c) and 2(d), respectively. Notice that, every time, the distribution of modes in the main energy bands is preserved. The overall effect of the tetragonal distortion is weak in the low- and intermediate-frequency ranges but affects strongly the modes originating from the high-energy manifold. Generally speaking, we notice (i) the hardening of all Γ_1 and Γ_5 symmetry modes, and (ii) the softening of the Γ_2, Γ_3, and Γ_4 frequencies. More in detail, we have found that the distortion affects drastically the Γ_4-Γ_5 doublet associated to Γ_{15}(ZnSe) and, to a lesser extent, the Γ_4-Γ_5 "CdSe"-like manifold. In both cases, the effect is opposite to our previous findings [compare, for instance, Fig. 2(c) with respect to Figs. 2(a) and 2(b), respectively]. This results in (i) an inversion of the Γ_4-Γ_5 splitting at 225 cm^{-1}, and (ii) a closing up of the Γ_4-Γ_5 gap at 175 cm^{-1}.

Including the anionic displacement is more complicated and does not result in a simple straightforward evolution of all modes which belong to the same symmetry. Remember that this internal distortion involves a shift of each anion, away from its ideal position at the centers of the tetrahedra. They move slightly towards the midposition of the lighter cations but, apart for small geometrical factors, most effects are included in the force constants. Quantitatively speaking, Fig. 2(d) shows that the geometrical part of this perturbation represents a minor correction as compared to the tetragonal distortion. The same is found when considering the eigenstates (see Table III).

To summarize, this simple model, which considers $AgGaSe_2$ as directly equivalent to $CdZnSe_2$, predicts correctly the experimental distribution of the optical phonons. Through successive perturbations, three bands develop. All modes in the high-energy band are associated to "ZnSe"-like vibrations. At low energy, the same is true for the highest $\Gamma_5[W_4]$ mode of the folded-acoustic branches. On the contrary, some modes ($\Gamma_4[W_2]$ in the intermediate range and $\Gamma_5[W_4]$ at low energy) are associated to pure "CdSe"-like vibrations. Finally, only three intermediate modes ($\Gamma_1[W_1]$, $\Gamma_3[X_3]$, and $\Gamma_5[W_3]$) together with the low-frequency $\Gamma_3[W_2]$ and the partner mode $\Gamma_4[W_2]$ show admixed contributions. They are the only ones which can be readily identified as folded modes of the pseudobinary II-VI compound $(Cd_{0.5}Zn_{0.5})$Se.

IV. THE REAL CRYSTAL: $AgGaSe_2$

Two major discrepancies appear when comparing the phonon energy spectrum obtained in the preceding section with the experimental results of Paper I. First, at high energy, the computed values range between 200 and 225 cm^{-1}: this is too low and, at the same time, the theoretical dispersion is too large. Compare, for instance, with the range of experimental values listed in Table II. On the contrary, at very low energy, the folded-acoustic components are not dispersive enough. The first discrepancy has a chemical origin: it occurs because we did not take properly into account the details of the bonding properties of $AgGaSe_2$ with respect to $CdZnSe_2$. The second occurs mainly from intrinsic limitations of the model which overestimates the lowest TA branch.

Consider first the chemical effect. It occurs because, in the real $A^{I}B^{III}C_2^{IV}$ material, three (gallium) and one (silver) electronic charges participate in the bond formation, instead of two for zinc and two for cadmium in the fictitious analog. There is, of course, some charge transferring from gallium to silver (through the common anions) in order to screen the point-ion perturbation and stabilize the lattice in the chalcopyrite structure,[1,2] but the net consequence that one would expect is to find all Ga—Se bonds stronger than their II-VI (ZnSe-like) counterpart. Similarly, all Ag—Se bonds should be weaker than their II-VI (CdSe-like) analogs. Of course, this simple picture neglects all changes in orbital shells and ignores p-d hybridization effects. As a matter of fact, it cannot easily be made quantitative. However, to check how much change in bond-stretching constant would be necessary to account for the specificity of $AgGaSe_2$, we have done a first calculation.

We follow the path of Ref. 11 and use only three parameters. Two are bond-stretching constants while the third one $\bar{\beta}$ accounts for all angular distortions. Performing a least-mean-squares fit to the 13 experimental Raman frequencies obtained in Paper I (see Table III of Paper I), we obtain the results listed in Table II (model I). We find now a factor of 2 between the bond-stretching constants associated to Ga—Se and Ag—Se bonds. This results in a better agreement with the experimental data. However, even if the stronger Ga-Se interaction rises up the high-energy band up to about 250 cm^{-1}, the width of this band is still too large. In this respect, there is no essential improvement when compared to the calculations performed for $CdZnSe_2$. In particular, it is worth noticing that, within the limitations of the model, only the inclusion of the geometric tetragonal compression gives again a positive crystal-field splitting for the highest-energy doublet Γ_5-Γ_4. At lower energy, we notice that, by using only one bond-bending constant, one closes severely the $\Gamma_5[W_4]$-$\Gamma_5[X_5]$ gap. In this case, the ratio of $E(\Gamma_5[W_4])/E(\Gamma_5[X_5])$ energies is about 1.2, which is just the square root of the quotient of Ag and Ga masses. This confirms well, in this crude approximation, the bending character of the restoring force constant: the two different cationic origins are then demonstrated by a consideration of Table III.

A better agreement with the experimental data can be found if we use four force constants, instead of only three, as fitting parameters. Performing again a least-mean-squares fit to the Raman-active frequencies of Paper I, we end up with the series of phonon energies listed in Table II (model II). At the expense of taking a negative value for β_2, we could reproduce fairly well the experimental results (see Fig. 2). This confirms our previous findings and shows that, in order to open the $\Gamma_5(W_4)$-$\Gamma_5(X_5)$ energy gap, a close association of the two different components with the different cations is needed. The negative value found for β_2 has no physical insight. What is more interesting is to find that β_1 is positive and much larger than β_2. The net consequence is the association of a strong AgSe-like character to the lowest $\Gamma_5(X_5)$ mode. Similarly, the $\Gamma_5(W_4)$ mode found at 80.3 cm^{-1} (an energy very close to the folding of the TA branch of ZnSe) is now mainly governed by GaSe-like vibrations with a negligible participation of the heavy cations (see Table III). In this case, no improvement was found in the high-energy range and we could not account, with this simple model, for the very narrow range of experimental frequencies (5 cm^{-1}, to be compared with about 40 cm^{-1} in most theoretical calculations). No attempt has been made to improve the calculation by taking into account different bond-bending force constants for the angular distortions with apex on the cations and the anions, respectively. This has been done for polar zinc-blende semiconductors[10] but, in our case, relaxing the conditions of equal bending parameters, one would end with seven parameters. Since, on the other hand, no attempt was made to account for the long-range Coulomb interaction, we have judged such refinements to be worthless.

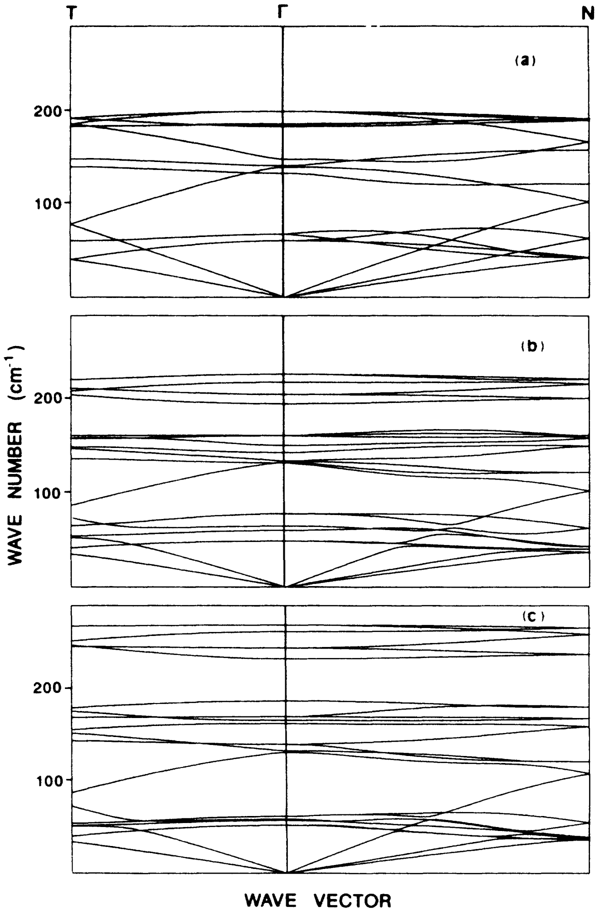

FIG. 3. Phonon dispersion curves computed in this work through the series of equivalent materials: (a) $(Zn_{0.5}Cd_{0.5})Se$; (b) $ZnCdSe_2$; and (c) $AgGaSe_2$ (model I).

For the sake of completeness, we give in Fig. 3 a comparison of the phonon dispersion curves computed in this work when using (a) the virtual cation $Zn_{0.5}Cd_{0.5}$ to describe the ZnS-like material $(Zn_{0.5}Cd_{0.5})Se$, (b) the fictitious chalcopyrite compound $ZnCdSe_2$, and (c) the real chalcopyrite $AgGaSe_2$ with only three parameters (model I).

To summarize, if the agreement with experimental results is fairly improved by the use of Keating models with three and four parameters for $AgGaSe_2$, the fundamentals of the accommodation of optic modes into three main bands are well accounted for by taking only the virtual chalcopyrite compound $CdZnSe_2$ and no adjustable parameters. This is an illustrative approach which contains most of the interesting physics.

V. CONCLUSION

We have used a simple approach to describe the optical phonons in $AgGaSe_2$. In the first approximation, we started from the folded-zone scheme and derived eigenvalues by considering $(Cd_{0.5}Zn_{0.5})Se$. This is the binary analog in which one virtual cation averages both cadmium and zinc species. In this case, we could not get satisfactory trends for the phonon energies. In a subsequent step, we included the specific cation ordering of the chalcopyrite structure and we described $AgGaSe_2$ in terms of the hypothetical (but more realistic) compound $CdZnSe_2$. This gave a correct repartition of modes in three bands and accounted for a progressive softening of CdSe-like modes ($\Gamma_4[W_2]$ and $\Gamma_5[X_5]$ frequencies), with respect to ZnSe-like ones. Finally, a better agreement with the experimental results was achieved by using the force constants as fitting parameters. In this case, an examination of the phonon energies and eigenstates, starting from the related binary materials ZnSe and CdSe, shows that all modes in $AgGaSe_2$ can be classified in three groups with (i) AgSe-like, (ii) GaSe-like, and (iii) mixed AgGaSe-like characters.

---

[1] J. E. Jaffe and A. Zunger, Phys. Rev. B **29**, 1882 (1984); also see **28**, 5822 (1983).

[2] J. Camassel, L. Artus, and J. Pascual, preceding paper, Phys. Rev. **41**, 5717 (1990).

[3] J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors: Growths, Electronic Properties and Applications* (Pergamon, New York, 1975).

[4] W. L. Roth, *Physics and Chemistry of II-VI Compounds,* edited by M. Aven and J. S. Prener (North-Holland, Amsterdam, 1967), Chap. 3.

[5] B. Hennion, F. Moussa, G. Pepy, and K. Kunc, Phys. Lett. **36A**, 376 (1971).

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

[7] M. Ya. Valakh, M. P. Lisitsa, G. S. Pekar, G. N. Polysskii, V. L. Sidorenko, and A. M. Yaremko, Phys. Status Solidi B **113**, 635 (1982).

[8] V. G. Plotnichenko, Y. A. Mityagin, and I. K. Vodopyanon, Fiz. Tverd. Tela (Leningrad) **19**, 2706 (1977) [Sov. Phys.—Solid State **19**, 1584 (1977)].

[9] P. N. Keating, Phys. Rev. **145**, 637 (1966).

[10] E. O. Kane, Phys. Rev. B **31**, 7865 (1985).

[11] M. Bettini, Phys. Status Solidi B **69**, 201 (1975).

[12] H. W. Spiess, V. Haeberln, G. Brandt, A. Rauber, and I. Schneider, Phys. Status Solidi B **62**, 183 (1974).