PHYSICAL REVIEW B VOLUME 60, NUMBER 18 1 NOVEMBER 1999-II

Ab initio study of the $\mathrm{Se_S}$ local oscillator in zinc sulfide

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(Received 1 September 1998; revised manuscript received 17 March 1999)

A method is presented to calculate the energy and symmetry of local vibrational modes (LVM's) at point defects in semiconductors from first principles. The force constants for the disturbed and undisturbed systems are calculated using a variant of the *direct approach*. The *ab initio* results are used as input parameters for a cluster simulation with up to 489 vibrating atoms, which accounts for hybridization effects between the LVM and the host lattice modes. The method is applied to the LVM of $\mathrm{ZnS{:}Se_S}$, which shows a pronounced fine structure due to both host and ligand induced isotope effects. The energy of the main peak, which represents the most abundant Selen isotope $^{80}\mathrm{Se}$, is calculated as 229.6 $\mathrm{cm^{-1}}$. This agrees very well with the result of 229.2 $\mathrm{cm^{-1}}$ from Fourier transform infrared experiments found in the literature. It is shown that the *ab initio* result improves the understanding of the LVM, when compared to the previously used *ad hoc* model, especially in the low-energy region. [S0163-1829(99)09525-9]

The aim is to calculate the energy and fine structure of a local vibrational mode (LVM) from first principles. In recent years, density-functional theory and density-functional perturbation theory have been used to calculate the phonon dispersion curves of a wide range of materials, including semiconductors and metals.[1–5]

For local vibrational modes, recent work has mostly focused on *ab initio* molecule simulations, again on a wide range of materials like fullerenes[6] or dicarbon defects in GaAs.[7] In Ref. 8, the LVM's in an organic adsorbate on a wolfram surface are calculated by simulating the wolfram single crystal using only one single atom. This approximation is correct if the frequencies of the eigenmodes of the adsorbate or impurity are much higher than the eigenmodes of the host lattice.

For ZnS:Se, the energy of the LVM is only 2 meV above the band edge of the accoustical phonon band. In this case, the hybridization of the LVM with host lattice modes must not be neglected, so that a large number of the atoms of the host lattice needs to be included in the calculation of the molecule. Such calculations with large molecules are not feasible with current computers. Therefore a two-step approach is used: First, force constants are calculated for the perfect and disturbed systems. Second, these force constants are used as input to a cluster simulation.

Several methods exist to calculate the interatomic force constants of a perfect crystal and the phonon-dispersion curves from first principles. In the *linear-response approach*, the effect of an infinitesimal displacement of the host atoms is studied by using the inverse dielectric matrix or by perturbation theory.[1] This requires two software programs: One to calculate the perfect system and one to calculate the linear response to a perturbation. In the *direct approach*, the linear response is obtained by using the same *ab initio* software to calculate the perfect system and the system where one atom has been moved slightly. The linear response is obtained by comparing the two results. If required, large displacements can be used to study anharmonic effects.

The easiest direct calculation is the *frozen phonon* approach: A snapshot of the displacement pattern of the phonon is imposed on a supercell. This is only possible, if the relative amplitudes of the vibrational mode are known *a priori*. For example, at special points of the Brillouin zone, the relative amplitudes can be deduced from symmetry principles. But this is not possible for arbitrary values of the wave vector $\mathbf{k}$, so that the frozen phonon approach is no longer applicable, unless a time consuming iteration procedure is accepted. The same is true for systems with a defect: The exact amplitude and direction of the vibration of the atoms around the defect is unknown, before the dynamical matrix has been solved.

To overcome the limited range of frozen phonon calculations, Frank, Elsässer, and Fähnle introduced the *direct force-constant approach*.[3] This uses a large supercell, where only one atom is displaced. Force constants are calculated within the linear approximation by dividing the change of the Hellmann-Feynman forces on the neighbors of the displaced atom by the amount of the displacement. However, in the plane-wave code used, a single displaced atom inside the supercell is equivalent to a superlattice of displaced atoms in full space. The range of the forces around the displaced atom can be visualized as spheres. The supercell must be large enough so that these spheres do not overlap.

Frank, Elsässer, and Fähnle applied their method to alkali metals. They calculated force constants for up to the fifth neighbor. They found that the force constants reduce rapidly with increasing distance. The heavier the alkali metal is, the faster is the decay. For natrium the ratio of next-neighbor to fifth-neighbor force constants is over 100:1, in the case of kalium, it is even over 500:1. This is due to the alkali metals forming a nearly free electron gas, which screens the effects of moving one ion efficiently.

In the case of ZnS, it is not sufficient to include only force constants for up to the fifth neighbor. In a test calculation, where the number of neighbors was reduced from 11 to 5, the frequencies of the acoustical vibrational modes changed by 5% at the X point of the Brillouin zone.

Calculations for ZnS are computationally much more expensive than alkali metal calculations, even if only the same number of neighbors is considered. Alkali metals have one valence electron pair for each two atoms. In the case of ZnS, the $3d$ electrons of Zn need to be treated as valence electrons, so that there are nine electron pairs for each Zn-S pair. The strongly bound $3d$ electrons require a high cutoff energy E_{cut} of 65 Ry, as compared to 8.5 Ry for the alkali metal calculations. Therefore the *direct force-constant approach* is not feasible for this work.

An alternative is the *planar force-constant separation approach* introduced by Wei and Chou.[2] It starts by calculating planar force constants. The supercell is formed by taking the primitive cell of the plane, for which force constants are calculated, and a vector perpendicular to that plane. This vector needs to be at least twice as long as the range of the interplanar forces. However, the other two sides of the supercell are small. This reduces the volume of the supercell, making the calculations less costly.

Planar force constants can be used to calculate the phonon dispersion among high-symmetry directions. To obtain the full dispersion from planar force constants, individual atom-atom force constants have to be separated. Each planar force constant is the sum of all force constants between the atoms in a plane and a given atom inside or outside that plane. As the force constants decay rapidly with increasing distance, Wei and Chou set all force constants to zero, if the distance between two atoms is larger than a cutoff radius r_{max}. The result is that each planar force constant can be written as a sum of a finite number of atom-atom force constants. This is a linear equation with a known left side (the planar constant calculated *ab initio*) and an unknown right side (the sum of atom-atom force constants). It is possible to calculate planar force constants for arbitrary space directions. Planar force constant for different space directions are different linear combinations of atom-atom force constants. The authors calculate so many planar constants that the system of linear equations becomes overdefined. Using a least-square fit, it is solved to obtain individual atom-atom force constants.

Wei and Chou applied the *planar force-constant separation approach* to silicon, which shows no long-range interaction between atoms. In compound semiconductors like ZnS, the long-range interaction has to be included as well. This is done by associating the Zn and S ions with an effective ionic charge. The force constants outside r_{max} are not set to zero, but are set equal to the dipole-dipole term of the interaction between those effective charges. The effective charge is determined by fitting the calculated dispersion curves to experiment. This is the only parameter not calculated directly from first principles.

Because of its special geometry, the planar force-constant separation method cannot be used to calculate LVM's at point defects. For these, the supercell must be large in all three space directions to reduce the defect-defect interaction to a minimum.

The method presented here is a generalization of the *direct force-constant approach* and the *planar force-constant separation approach*. An analysis of the work of Wei and Chou shows that at no point in their work are their special geometries actually required. Results for any arbitrary supercell can be used as input to the separation approach. Moving one atom of a supercell is equivalent to displacing a superlattice of atoms in real space. The Hellmann-Feynman forces acting on a given atom of the supercell are a superposition of the interactions of that atom with the superlattice of the displaced atoms. If a cutoff radius r_{max} is introduced, only a finite subset of the superlattice has to be considered. For each atom in the supercell, a linear equation can be written for the interaction of that atom with the finite subset. If enough supercells are calculated, the system of linear equations becomes overdefined and can be solved for individual atom-atom force constants using a least-square fit.

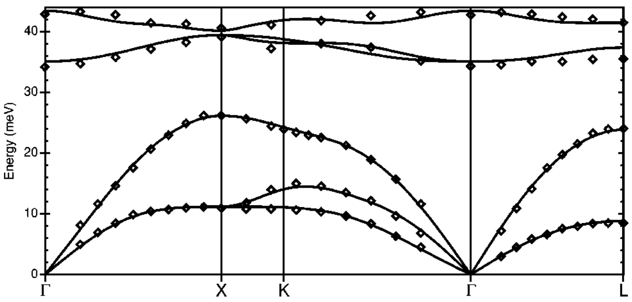

FIG. 1. *Ab initio* results (solid lines) for the phonon-dispersion curves of ZnS, compared to experimental results from neutron scattering (diamonds, Ref. 12).

To calculate the dispersion curves of ZnS, three different supercells containing 40, 48, and 56 atoms are used. For each supercell, 12 calculations are performed. In each calculation, one atom is displaced by 0.06 a_0 in the positive or negative x, y, or z direction, where a_0 is the Bohr radius. These results are used as input to the separation procedure, which is used to calculate force constants for up to the 11th shell of neighbors for both Zn and S. The effective charge is determined as 0.86 e for Zn and -0.86 e for S by fitting the split of the TO and LO phonon at the Γ point. The resulting phonon dispersion curves are plotted in Fig. 1. To test convergency, force constants are calculated for up to the 18th shell, but no significant difference is found in the resulting phonon dispersion curves.

For the disturbed ZnS:$\mathrm{Se_S}$, a bcc supercell with 32 atoms is used. The cell is oriented such that the S atom is at the origin and the four Zn ligands are located at $(-a/4,-a/4,-a/4)$, $(a/4,a/4,-a/4)$, $(a/4,-a/4,a/4)$, and $(-a/4,a/4,a/4)$ with a as the lattice constant of 10.22 a_0. After the central S has been replaced with Se, it is necessary to calculate the relaxation to find the new equilibrium positions of the atoms around the defect. Only symmetry conserving relaxations are considered. The first shell of Zn neighbors are moved along the line of the Se-Zn bonds by 0.19 a_0 away from the Se atom. The S atom at $(a/2,a/2,0)$ is moved by $(0.028a_0,0.028a_0,0.005a_0)$. The other 11 S atoms in the second shell are moved accordingly. Because movement is already low in the second shell, no further shells are relaxed. The results from this and previous work[9] show that for movements of up to $0.06a_0$, the error due to anharmonicity is smaller than or in the same range as the errors due to the other approximations used (local-density approximation, energy cutoff, pseudopotentials, and so on).

After relaxation has been completed, the force constants of the disturbed system are calculated using the direct force-constant approach. The separation method discussed above is not applicable here, because changing the supercell geometry will also change the distribution of the impurities in the *ab initio* calculation. Therefore only force constants between the

TABLE I. Energy of the ZnS:Se LVM versus cluster size. The impurity is ^{80}Se. The mass of the Zn ligands is set to 65.38 *u*, the average mass of Zn. In this case, a triplet T_2 mode is expected. Small clusters lead to an artifical line split, which is indicated by giving a range like 28.364 . . . 28.392 as result.

Number of shells	6	7	8	9	12	14	18	21	25
Number of atoms	47	71	87	99	159	191	293	381	489
Calculated energy [meV]	28.364 . . . 28.392	28.283 . . . 28.297	28.322	28.293	28.299	28.302	28.294	28.289	28.289

impurity and its first- and second-nearest neighbors are determined by displacing the Se impurity by 0.02 a_0 and 0.05 a_0 in the positive and negative z directions in four different *ab initio* calculations. The change of the force constants between the Zn ligands and their respective first- and second-nearest neighbors is obtained by displacing one of the four nearest neighbors of the Se impurity by 0.04 a_0 along the positive or negative x, y, and z axis in six additional calculations. All other force constants are not changed.

The LVM is calculated using the cluster method. It consists of a classical simulation of vibrating point masses. The cluster contains all atoms inside a certain cluster radius with the impurity located at the center. The mass of all atoms outside the cluster is set to infinity, so that these atoms do not move. The force constants for the interaction of the atoms inside and outside of the cluster are not neglected.

The dynamical matrix is diagonalized to calculate the vibrational modes of the cluster. The eigenvalue of a particular mode is the square of its frequency. The squares of the elements of an eigenvector give the spatial distribution of the vibrational energy. If at least 35% of the energy is located on the impurity and at least 70% are located on the impurity and its four neighbors, the mode is considered a local vibrational mode.

To test convergency, the cluster size is varied between 47 and 489 atoms; see Table I. It is found that increasing the cluster size from 99 atoms to larger sizes changes the calculated energy of the LVM by less than 10 μeV.

ZnS:Se shows a pronounced fine structure, which can be resolved using Fourier transform infrared (FTIR) spectroscopy.[13] This fine structure is due to isotope effects: There are six stable isotopes for the Se impurity and five isotopes for the Zn ligands. Each possible isotope combination gives an LVM with a slightly different energy. If all Zn ligands have the same mass, a threefold degeneracy is observed. This triplet splits into one singlet and one doublet, or three singlets if the Zn ligands have different masses. There are five stable Zn isotopes, so that $5^4 = 625$ combinations are possible for the Zn ligands. Due to the tetrahedral symmetry, many of these combinations are equivalent, so that only 70 independent configurations remain.

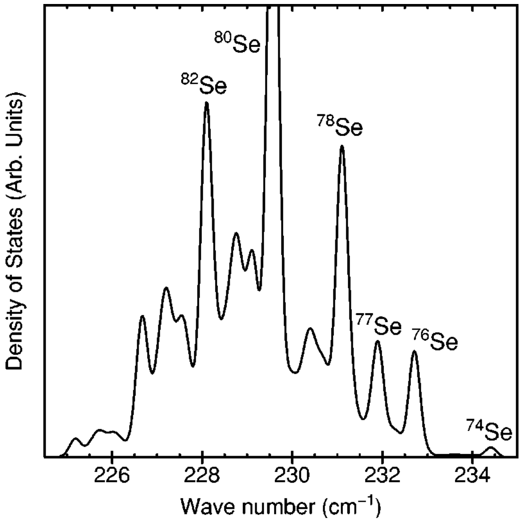

FIG. 2. Theoretical fine structure of the LVM in ZnS:Se. The calculated phonon frequencies have been broadened by Gaussians with a half-width of 22 μeV = 0.18 cm^{-1}.

For each of the six possible Se centers, all 70 ligand combinations are solved, so that there are 420 cluster calculations in total. Each calculation results in three possibly degenerate modes. At the energy of each LVM, a Gaussian curve is drawn. All Gaussians have the same half-width, which is fitted to the experiment. The amplitude of each Gaussian is set to the natural abundancy of the isotopes used in the cluster calculation for that Gaussian.

The FTIR results from Ref. 10 and the calculated fine structure are printed in Figs. 3 and 2. The location and the relative amplitude of the main maxima, which are labeled ^{76}Se through ^{82}Se, are reproduced very well. However, the intensity of the calculated side maxima is lower than in the experiment. The closer a side maximum is to the main peak ^{80}Se, the bigger is the deviation. This can be explained if a

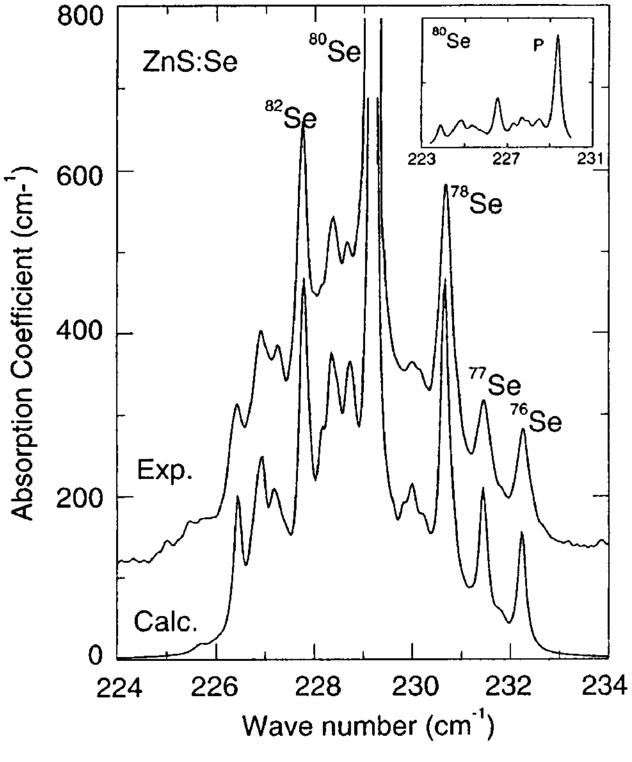

FIG. 3. Experimentally observed fine structure of the LVM in ZnS:Se, taken from Ref. 10.

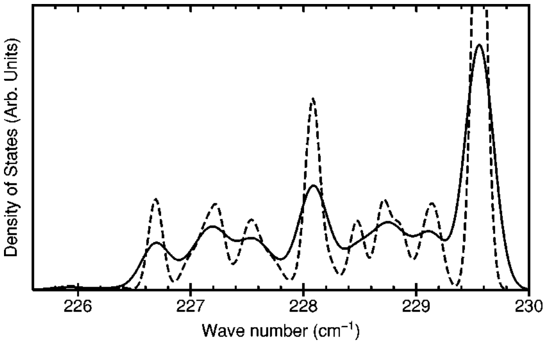

FIG. 4. Theoretical fine structure of the LVM, if only ^{80}Se is present. The solid line uses a half-width of 22 μeV=0.18 cm^{-1}, while the dashed line has been calculated with 11 μeV =0.09 cm^{-1}.

certain percentage of the impurities in the experiment has a non-Gaussian broadening of the associated LVM. For example, Se impurites located next to other Se impurities or intrinsic crystal defects have a slightly different energy. If a hole or electron is bound to a certain percentage of the Se impurities, their LVM will be broadened by the electron-phonon interaction.[11]

The calculated fine structure is about 0.5 cm^{-1} wider than experimentally observed. This is due to the limited cluster size. By setting the atoms outside of the cluster as immobile, a hard cluster wall is introduced, which reflects any outside amplitude of the LVM back into the cluster. This increases the vibration amplitudes and therefore the isotope shifts inside the cluster slightly.

Sciacca *et al.*[10] presented a model calculation for ZnS:Se. They used their model to predict the fine structure for doping with ^{80}Se, the most abundant Selen isotope. The result shows two prominent peaks, which are 0.34 meV apart; see the inset in Fig. 3. The results of this work for ^{80}S are plotted in Fig. 4. The solid line is calculated with a half-width of the Gaussians of 22 μeV, the same as in Fig. 2. For the dashed line, the half-width of the Gaussians is reduced to 11 μeV. The shape of this dashed line agrees with the model results of Sciacca *et al.* in Fig. 3. However, the energy difference between the main maxima and the highest side maxima is 0.18 meV in this work, as opposed to 0.34 meV in Ref. 10.

In Fig. 2, the difference between the ^{82}Se and ^{80}Se maxima is 0.18 meV. This means that the side maximum of the ^{80}Se peak (see Fig. 4) and the ^{82}Se fall on top of each other. The same is true for the side maximum of ^{78}Se and the maximum of ^{80}Se and so on. In Ref. 10, the difference between the maximum and side maximum is calculated as 0.34 meV; see Fig. 3. This means that the side maximum of ^{78}Se is located below the maximum of ^{82}Se and so on.

This hiding of important side maxima below other maxima makes it difficult to find the actual relationship between the Se isotope shift and the Zn isotope shift without *ab initio* calculations. In Ref. 10, the calculated fine structure does not match the experimental results in the region 225–226 cm^{-1}. As the intensity is low in that region, it is difficult to distinguish between experimentally observed noise and inappropriate interpretation of the spectrum.

In conclusion, a method has been presented to calculate the energy and the fine structure of LVM's from first principles, which include hybridization effects. The results show clearly that models are not trustworthy for fine-structure calculations of LVM's if a large number of isotope combinations is involved. The calculations presented here agree better with the FTIR experiments in the low-energy region than the model presented by Sciacca *et al.*[10] The model and the calculation completely disagree on the results found for ZnS:^{80}Se. While the model results might be wrong due to the difficult assignment of the lines, the presented *ab initio* results are unambiguous. Therefore such *ab initio* calculations should be used to explain complicated fine structures.

The author thanks U. Scherz for many fruitful discussions and for his encouragement. The author wishes to thank the Fritz-Haber Institut, Berlin, for providing their computer programs FHI93CP and FHI94MD.[13] The author also thanks the Konrad-Zuse-Zentrum für Informationstechnik, Berlin for providing CPU time and support for a Cray T3D massive parallel system.

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