

# Temperature dependence of band gaps in semiconductors: electron-phonon interaction

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In the past decade a number of calculations of the effects of lattice vibrations on the electronic energy gaps have been performed using either semiempirical or *ab initio* methods. This work has led to the realization that the lowest gaps usually decrease with increasing temperature whereas in a few exceptional cases the opposite development is also observed.[1]

Most of the experimental results for the temperature dependence of gaps have been obtained for elemental or binary semiconductors.[1] Lately, however, ternary materials such as those with chalcopyrite structure have begun to be investigated. Among the chalcopyrites under examination are II-IV-V<sub>2</sub> compounds (e.g. ZnGeAs<sub>2</sub>) and those in which the divalent cation is replaced by either monovalent copper or silver (e.g. MGaX<sub>2</sub>, M = Cu, Ag; X = S, Se, Te). Whereas the temperature dependence of the energy gaps of the II-IV-V<sub>2</sub> compounds exhibits the standard behavior, i.e. a monotonic decrease with increasing temperature, Cu and Ag chalcopyrites often show non-monotonic temperature behavior with a maximum at low temperatures followed by a decrease or sometimes an extended flat plateau at low temperatures. In the literature the drop of the electronic gap below the maximum has often been ascribed to the combined effect of thermal expansion and the volume dependence of the gap. However, neither has a convincing scheme been suggested to understand the occurrence of the low-temperature gap decrease nor has a quantitative picture for the magnitude of the gap decrease been developed on the basis of the volume dilation mechanism. On the other hand, temperature dependent effects due to the presence of the *d*-like valence electrons (3*d* for Cu and 4*d* for Ag) and their admixture with the usual *p*-like counterparts (e.g. 4*p* for Se, 5*p* for Te) are generally ignored. The observation that the non-monotonic temperature dependence is particularly manifest in the chalcopyrites involving Ag 4*d*-valence electrons led us to suggest that this effect is related to *p*-*d*-electron hybridization. A first estimate of the degree of valence electron hybridization can be surmised by comparing the difference of the relevant valence electron energies of the various elements involved.[2] Figure 1 reveals that in case of Zn and Cd the *d*-levels are lifted in energy, being considerably separated from the occupied *p*-levels whereas there is a close proximity of the *d*-levels of Cu and Ag to the *p*-levels of the chalcogen atoms enabling enhanced *p*-*d* hybridization.

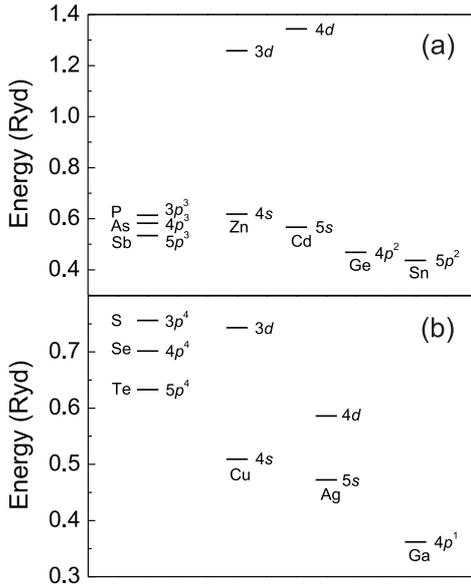


Figure 1: Relevant valence electron energies of the various elements in the chalcopyrite compounds according to Ref. [2]. (a) MYX<sub>2</sub> (M = Zn, Cd; Y = Ge, Sn; X = P, As, Sb). (b) MGaX<sub>2</sub> (M = Cu, Ag; X = S, Se, Te). Note the proximity of the 3*d* and 4*d* energy levels of Cu and Ag to the valence *p*-levels of the chalcogenides.

The temperature dependence of the energy gap is due to the electron-phonon interaction which depends critically on the amplitude of the phonons and the corresponding coupling constants. Unfortunately, because of computational complications related to the size of the unit cell and *k*-point convergence issues, calculations of the corresponding electron-phonon interaction coefficients are difficult and rare. The phonon amplitudes, however, are accessible with great precision from *ab initio* calculations of the electronic structure. Recently, we have

studied the lattice and thermal properties of  $\text{CuGaS}_2$  in more detail by means of *ab initio* calculations.[3] Applying analogous computational techniques we have now extended these calculations and obtained the phonon dispersion relations and the phonon density of states of  $\text{AgGaX}_2$  ( $X = \text{S, Se, Te}$ ) as well as of  $\text{MYX}_2$  ( $M = \text{Zn, Cd; Y = Ge, Sn; X = P, As, Sb}$ ) as reference materials.[4]

Figure 2 shows the total and the partial phonon density of states of the  $\text{AgGaX}_2$  chalcopyrites obtained from *ab initio* calculations using the PBEsol ansatz for the exchange correlation functional which we have also utilized in a preceding investigation to obtain the low-temperature specific heats of several chalcopyrites.

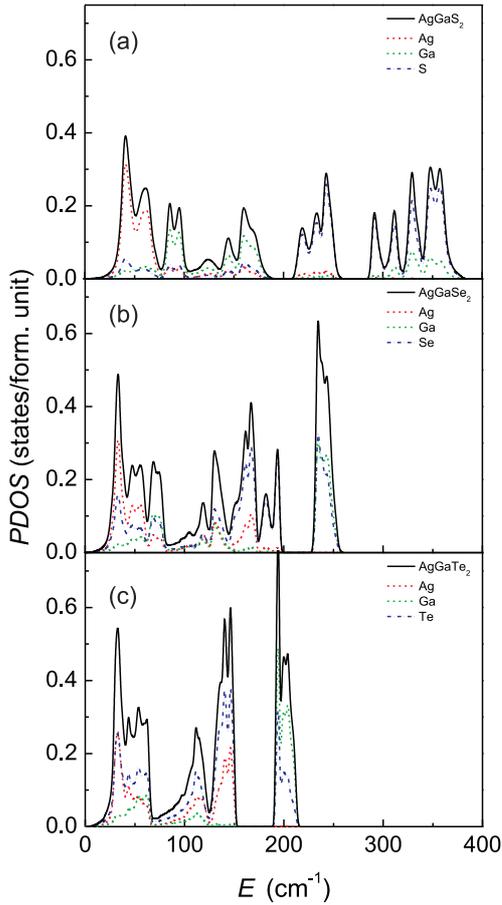


Figure 2: Total and partial phonon densities of states (PDOS) of the chalcopyrites  $\text{AgGaX}_2$  ( $X = \text{S, Se, TE}$ ) as obtained from VASP PBEsol calculations. The (red) dashed line represents the partial PDOS of Ag.

In view of the finding that the low-energy phonon spectrum and the density of states is dominated by Ag related vibrations we have re-analyzed literature data and new highly-resolved non-monotonic temperature dependence gap versus temperature measurements e.g. for  $\text{AgGaX}_2$  ( $X = \text{S, Se, Te}$ ) by fitting a model proposed by Göbel *et al.* for  $\text{CuX}$  ( $X = \text{Cl, Br}$ ).[4] Using two Bose-Einstein oscillators with weights of opposite sign leading to an increase at low temperatures which towards higher temperatures is finally dominated by the stronger decrease.

The temperature dependence of the energy gap is given by

$$E(T) = E_0 + \sum_i A_i [2n_{\text{BE}}(E_i/k_{\text{B}}T) + 1], \quad (1)$$

where  $A_i$  are the weights which, if negativ, describe the degree of the energy decrease with increasing temperature and  $n_{\text{B}}$  is the Bose-Einstein factor:

$$n_{\text{BE}}(E_i/k_{\text{B}}T) = 1/(\exp(E_i/k_{\text{B}}T) - 1). \quad (2)$$

Without any further assumption about thermal expansion terms, by including a second low-energy Bose-Einstein oscillator this model accounts well for the non-monotonic temperature dependence of the gaps with the effects of the two oscillators on the gap having different signs, i.e. the low-energy oscillator securing an increase of the gap with increasing temperature.

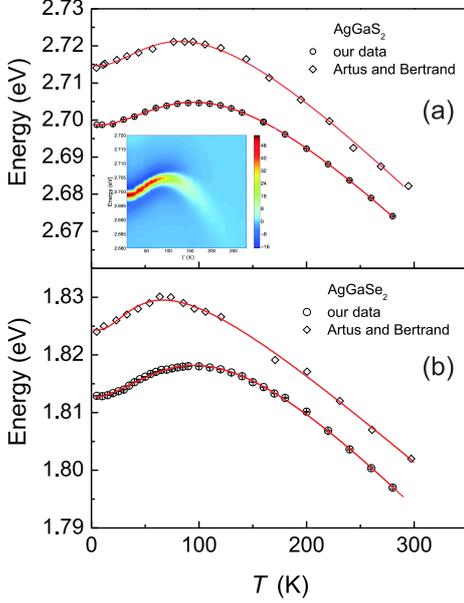


Figure 3: Temperature dependence of the gap energy of (a)  $\text{AgGaS}_2$  (our data and those of Artus and Bertrand (1987) and (b)  $\text{AgGaSe}_2$ . The (red) solid lines represent the fits to Eq. (1) assuming two Bose-Einstein oscillators. The inset in (a) displays the temperature evolution of the wavelength modulated reflectivity spectrum.

Figure 3 displays the energy gaps of  $\text{AgGaS}_2$  and  $\text{AgGaSe}_2$  together with the fits of Eq. (1) to literature and our new experimental data. Especially the improvement of temperature resolution at low temperatures clearly reveals that the gaps level off for  $T \rightarrow 0$  K with no indication of a linear term due to a lattice expansion contribution. The highly resolved data also enabled reliable fits of the temperature dependence at low temperatures. Without any constraints the fits converged to energies of the Bose-Einstein oscillators which differ by almost an order of magnitude. The decrease of the gap at high temperatures is described by a Bose-Einstein oscillator energy corresponding to  $\sim 400$  K which matches very well to optic phonons branches essentially due to S or Se vibrations (see Fig. 2).

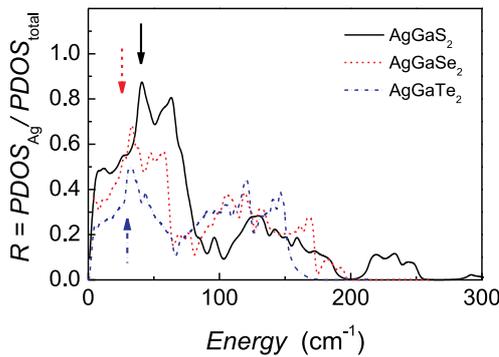


Figure 4: Ratio of the partial PDOS of Ag w.r.t. the total PDOS of  $\text{AgGaX}_2$  ( $X = \text{S, Se, Te}$ ), with (black) solid, (red) dashed and (blue) dash-dotted line, respectively. The vertical arrows indicate the energies of the second low-energy Bose-Einstein oscillator ( $E_2$ ) obtained by fitting the temperature dependence of the energy gaps with Eq. (1).

Inspection of the partial phonon density of states of the chalcopyrites  $\text{AgGaX}_2$  ( $X = \text{S, Se, Te}$ ) reveals that the low-energy part of the phonon spectrum is essentially dominated by acoustic zone-boundary phonons related to Ag vibrations (see Fig. 4). It turned out that the frequencies of the Bose-Einstein oscillators which describe the decrease of the gap below the maximum agree well with these Ag peaks in the phonon density of states. This result renders strong support to our proposal that the non-monotonic temperature dependence of the energy gap is closely related to  $d$ - $p$  electron hybridization.

We hope that the systematic analysis presented here will encourage theorists to tackle the peculiar temperature dependence of the electronic gaps of semiconductors involving *d*-electron atoms (e.g. Cu or Ag). Measurements at low temperatures using crystals with pairwise replacement of isotopes (e. g.  $\text{AgGa}^{32}\text{S}_2$  -  $\text{AgGa}^{34}\text{S}_2$ ;  $\text{Ag}^{69}\text{GaS}_2$  -  $\text{Ag}^{71}\text{GaS}_2$ ;  $^{107}\text{AgGaS}_2$  -  $^{109}\text{AgGaS}_2$ ) are underway in order to separate the individual effects of the various atoms on the zero-temperature gap renormalization.

**References:**

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