# Optical Reflectivity and Band Structure of $ZnS_{1-x}Se_x$ Mixed Crystals*

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Optical reflectivity measurements on mixed crystals of the system $ZnS_{1-x}Se_x$ $(0 \leq x \leq 1)$ were made at room temperature in the energy region of 2.5 to 9.5 eV. Indirect as well as direct optical transitions were observed in the $\epsilon_2$ spectra computed by a Kramers-Kronig analysis. Considering the complete series of mixed crystals, the very complex structure of the observed spectra can only be explained assuming separated energy bands for the different components of these mixed crystals.

Optical investigations of mixed crystals conducted during the past several years showed the existence of two types of mixed crystals with regard to their electronic properties. The first one, called the persistence type, has separated electronic energy bands belonging to the corresponding components of the mixed system. These separated bands are explained by a local optical excitation, i.e., Frenkel excitons. This type of energy band was found in halogen-substituted alkali halides.[1,2] The second type of mixed crystals, called the amalgamation type, seems to have only mixed (amalgamated) energy bands for the corresponding different components. The majority of mixed crystals investigated has been connected to the latter band type.[3-13] In this Letter, however, we report results of optical reflectivity measurements on the system $ZnS_{1-x}Se_x$, which can be explained only assuming the persistence type.

The crystals were grown by an iodine vapor-transport technique and showed cubic structure. The source materials were mixed ZnS and ZnSe powders. The molecular fraction $x$ varied in the region $0 \leq x \leq 1$. The compositions of the mixed crystals were determined by x-ray fluorescence measurements to an accuracy of 0.1 mole%. Reflectivity measurements at room temperature were made at nearly normal incidence in the energy region of 2.5 to 9.5 eV continuously by a vacuum spectrometer. $\epsilon_2$ has been computed by a Kramers-Kronig analysis using the reflectivity data.

Figure 1 shows typical $\epsilon_2$ spectra for some $ZnS_{1-x}Se_x$ crystals of different compositions. The energetic positions of peaks and shoulders in these spectra, marked by vertical lines, vary systematically with the composition. The striking feature of these spectra is the distinctness of the observed structure. The numerous peaks and shoulders definitely suggest the existence of separated bands. The peaks at 3.71 and 3.78 eV observed in the spectra of the mixed crystals up to a molecular fraction of $x=0.8$ (see also Fig. 2) are noted as a spin-orbit-split transition $\Gamma_{15}$-$\Gamma_1$ in pure ZnS. In analogy, some peaks in the region of 7 eV can be attributed to transitions well known in pure ZnS (Fig. 2). Considering the complete series of the mixed crystals, the com-

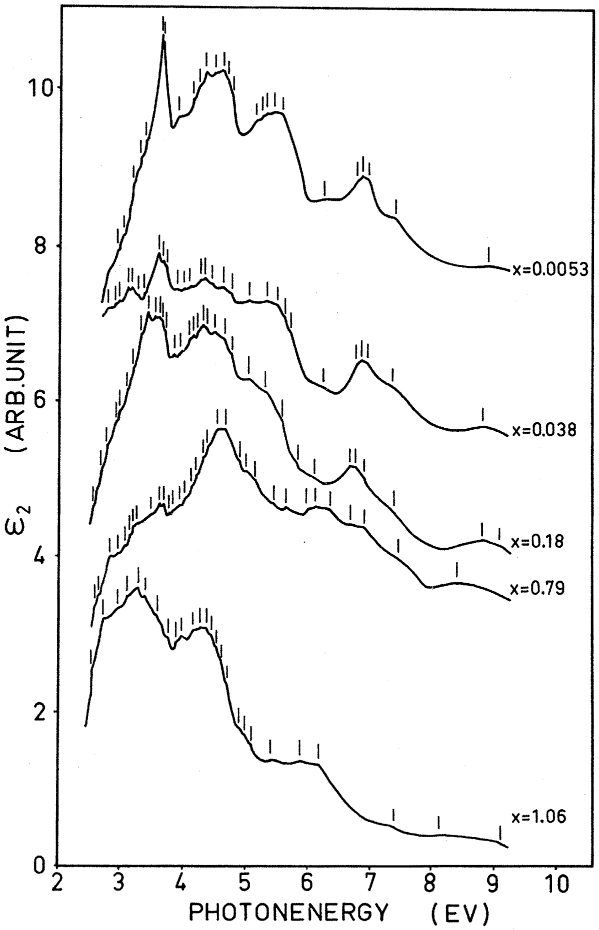

FIG. 1. $\epsilon_2$ spectra for some $ZnS_{1-x}Se_x$ mixed crystals.

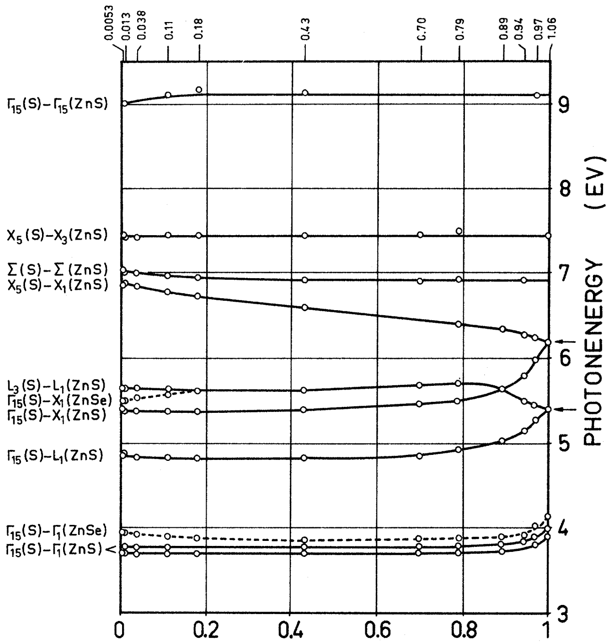

FIG. 2. Transitions from S bands versus composition.

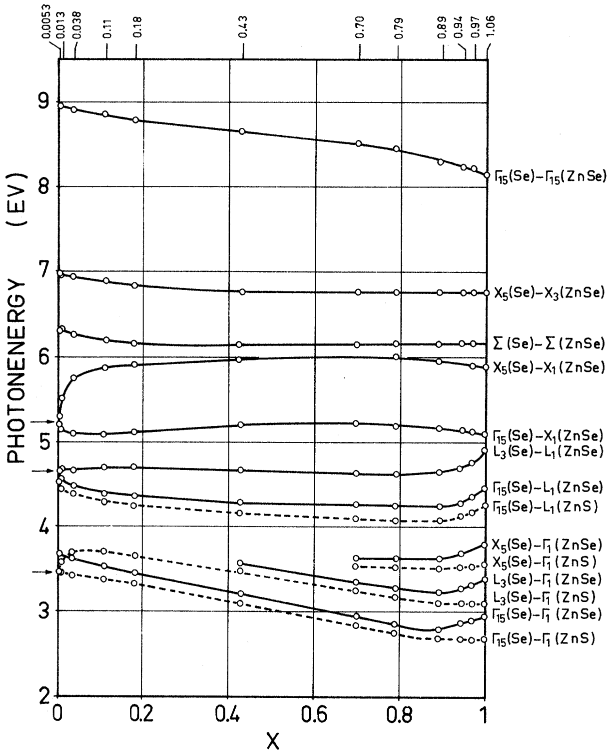

FIG. 3. Transitions from Se bands versus composition.

plex structure of the observed spectra can only be explained as follows: (1) The crystals belong to the persistence type. (2) The Zn bands are split into two bands with an energy separation of about 0.3 eV due to the different neighbors of the Zn atoms, i.e., S and Se, respectively. (3) Indirect as well as direct optical transitions are observed.

According to these assumptions direct and indirect optical transitions are possible from S or Se valence bands to both Zn conduction bands. The energetic positions of these different optical transitions, depending on the molecular fraction $x$ of the $ZnS_{1-x}Se_x$ mixed crystals, are shown in Fig. 2 (transitions from S bands). The terms (ZnS) and (ZnSe) in Figs. 2 and 3, respectively, characterize the two types of conduction bands. A systematic shift of the different transitions from the different valence bands to the conduction bands may be noted.

Regarding the $k$ independence of impurity bands at low concentration of the substituent atoms, it is possible to distinguish between direct and indirect transitions, if the complete series of mixed crystals are included. In Fig. 2, for example, the energetic distance between both the direct transition $X_5(S)$-$X_1(ZnS)$ and the corresponding indirect transition $\Gamma_{15}(S)$-$X_1(ZnS)$ becomes smaller with decreasing S concentration, i.e., with increasing molecular fraction $x$. At low S concentrations the S valence band becomes $k$ independent and forms a localized S term (arrows in Fig. 2). As shown in Fig. 3 the Se valence band behaves analogously. By extrapolation we have found the indirect transitions for pure ZnS and pure ZnSe, never reported before. Furthermore, the complex structure of pure ZnSe may be interpreted.

The experimental results imply absolute band structures for the complete system of $ZnS_{1-x}Se_x$ mixed crystals. These absolute values definitely are of great interest in the adjustment of parameters in semiempirical band-structure calculations; furthermore, they may be employed to prove band-structure calculations from "first principles" methods. Perhaps our results can stimulate the theoretical workers to intensify discussions concerning mixed crystal systems.

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# Soft Transverse Phonons in a Metallic Glass

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The acoustic properties and low-temperature specific heat of a dense metallic glass in bulk form have been studied for the first time. A large softening of long-wavelength transverse acoustic phonons in $Pd_{0.775}Si_{0.165}Cu_{0.06}$ glass, relative to the crystal, is observed which is not simply attributable to the small density difference between the two states.

The understanding of the glassy metallic state has been impeded, in large part, by the inability to prepare bulk specimens of glassy (or amorphous) metals.[1] We report here the first results of ultrasonic and low-temperature specific-heat experiments on a metallic glass.[2] These investigations were made possible by our ability to produce a glassy metal in bulk form. We observe a striking "softening" of long-wavelength transverse acoustic phonons in the glass relative to the crystal, which is not simply attributable to the small density difference between the two states.[3] These findings have significance for our understanding of superconductivity in amorphous metals as well as our understanding of the glassy metallic state.

The experiments were performed on $Pd_{0.775}Si_{0.165}Cu_{0.06}$ cylinders, 1 to 2 mm in diameter.[4] The glassy phase was obtained by rapid quenching of the melt, which was contained in a quartz capillary. A fine-grained ($\lesssim 10\ \mu m$) polycrystalline sample, consisting of the initial metastable crystalline structure,[5] was prepared by heating the glass to 673 K for 16 min. Longitudinal and transverse sound velocities were measured by MHz-pulse techniques on samples 1 to 2 cm in length. Low-temperature specific heats were measured in an adiabatic calorimeter between 1.8 and 20 K using standard discontinuous heating methods. Mass densities were obtained by weighing in $CCl_4$ and air at room temperature.

We analyzed the low-temperature specific heat, Fig. 1, by fitting to it a polynomial of the form $C = aT + bT^3 + dT^5$ using a least-squares procedure. Since the effective Debye temperatures $\Theta(T)$ for glass and crystal exhibited a strong tem-

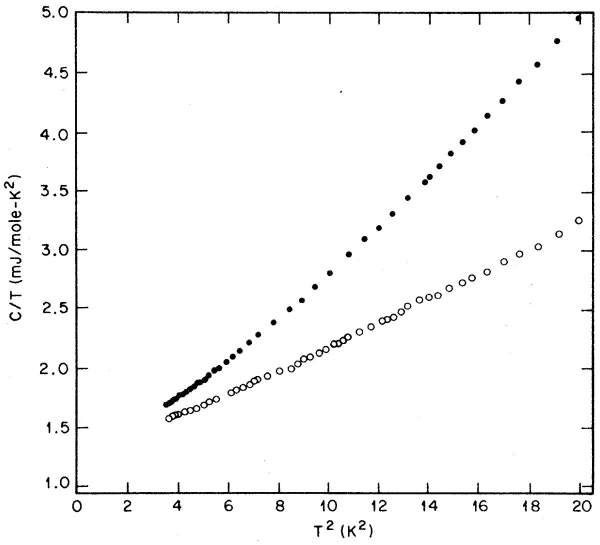

FIG. 1. Specific heats $C$ of glassy and crystalline $Pd_{0.775}Si_{0.165}Cu_{0.06}$. Linear plot of $C/T$ versus $T^2$ for glass (closed circles) and crystal (open circles).