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Author
Camassel, J.

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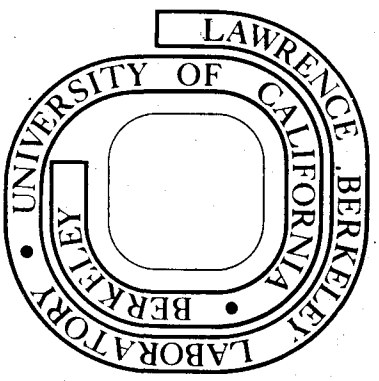

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J. Camassel*, M. Schluter**, S. Kohn, J. P. Voitchovsky†,
Y. R. Shen and M. L. Cohen§

Physics Department
University of California
Berkeley, California

and

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California

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†Swiss National Science Foundation fellow.

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OPTICAL PROPERTIES OF LAYER COMPOUNDS

GaS_xSe_{1-x}

J.CAMASSEL*, M. SCHLUTER§χ, S. KOHN, J.P. VOITCHOVSKYα, Y.R. SHEN and M.L. COHEN§

Department of Physics, University of California and
Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720.

We present an investigation of the reflectivity and wavelength modulated reflectivity of GaS_xSe_{1-x} mixed crystals at 5° K for energies ranging from 3 to 6 eV. The main structures in the optical response function of the alloy spectra are found to exhibit three characteristic classes of shift versus composition. These results are discussed on the basis of a new, slightly modified, pseudopotential band structure calculation for GaSe. The anisotropic and excitonic character of the 3.4 eV structure in GaSe is also discussed in light of the band structure calculation.

1. INTRODUCTION

The semiconducting III-VI compounds GaS and GaSe crystallise in the layer structure of Fig. 1. The structure is clearly 2-dimensional and the crystals exhibit highly anisotropic mechanical properties. However not all electronic states reflect this anisotropy. With alloying three different kinds of regular stacking for adjacent layers (i.e. three different polytypes) occur. The change from one to a different polytype give rise to specific effects[1]. We have investigated the shift from GaSe to GaS of the main interband transitions and focus on 3 particular points : i) we find specific effects connected with the bond Ga-Ga, ii) we study atomic-like properties of most electronic levels in GaS_xSe_{1-x} and iii) we present an identification of the 3.4 eV "hyperbolic exciton" of GaSe. Other experimental works on GaS_xSe_{1-x} alloys include absorption[1], resonant[2] or non-resonant[3] Raman scattering and luminescence[4] studies. For a complete discussion of the band structure and optical properties of GaSe, we refer to the work

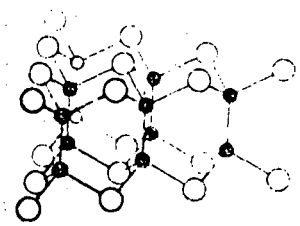

Fig.1. A constitutive layer of GaS (Se) crystals.

of Ref. 5. The experimental set up is described in Ref.6.

2. TRANSITIONS WITH STRONG CATION CHARACTER AND ZERO ENERGY SHIFT.

We find 4 structures belonging to this class of shift. Their energy is shown in Fig. 2 as a function of composition. The label G stands for predominant Gallium-character in the wave function and they show no overall shift if sulphur is substituted for Selenium.

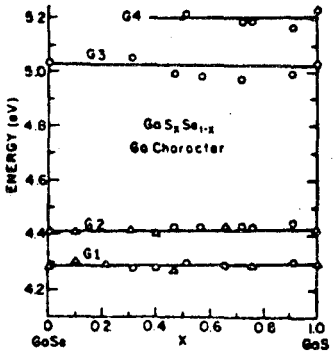

Fig.2. Energy diagram of the Ga-Ga transitions

A plot of the charge density contours is given in Fig.3. for both initial and final states together with the connecting transition function F_z which gives a real space localisation of the transition. As seen from the charge density contours, the charge in both initial and final states is concentrated in the vicinity of the Gallium atom. Little charge sits around the anion and the transition function also exhibits a strong localisation on the Gallium atom.Obviously these localisations explain the negligeable shift of the G transitions when Sulphur is substituted for Selenium. These transitions are believed to be caused by the particular crystal structure where like-atom bonds (cation-cation) exist. No zero shift transitions are found in the zinc-blende alloy systems which have alternative anion-cation arrangements.

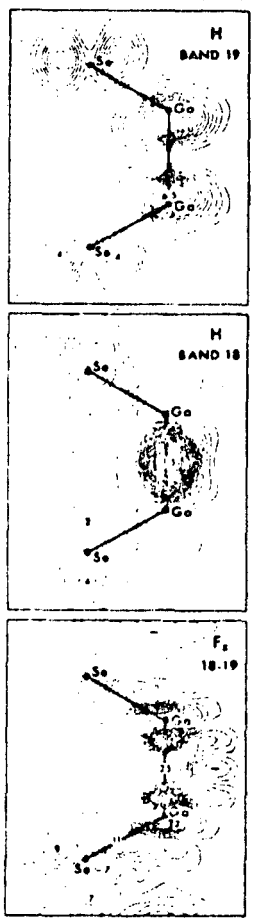

Fig. 3 Charge density contour plots for the G_1G_2 transitions.

3. TRANSITIONS WITH STRONG ANION CHARACTER AND A STRONG ENERGY SHIFT.

We find again 4 transitions belonging to this class of shift (see Fig. 4). We shall discuss only the lower one (S_1) which corresponds in GaSe with a very narrow peak reported in absorption[7] around 3.4 eV. In Fig. 5-d, we show a low temperature reflectivity spectrum obtained on our best sample. The excitonic characters of the S_1 transition is quite obvious and a very narrow doubled is resolved at 3.37-

3.40 eV, at 5° K. We can give an unambiguous assignement of this transition. It corresponds with an excitation of electrons from the second pair of valence band Γ_{5-} to the lower conduction band Γ_3^+. We calculate the corresponding anisotropy parameter[5] and from standard theories of anisotropic excitons for Mo critical points, we get a theoretical binding energy E_B^{cal} = 30 meV. On the other hand, we measure an experimental splitting at low temperature E_B^{exp} = 30 ± 5 meV which is in excellent agreement with the calculated value and completely supports the model. So we conclude that a 3-dimensional, anisotropic, M_o c.p. with a 30 meV binding energy is responsible for the sharp 3.4 eV structure in GaSe. The possibility of an additional spin-orbit partner within ∿ 0.3 eV is compatible with i) the Γ_{5-} assignement, and ii) the electro-reflectance results of Fig.5-b.

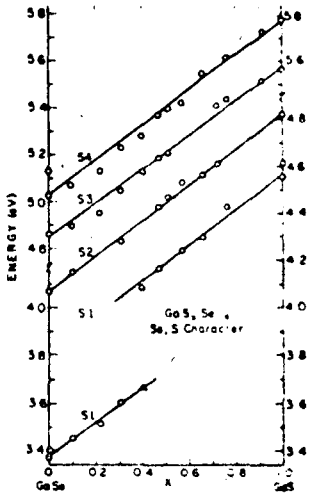

Fig.4 Energy diagram of the S(Se) transitions.

With alloying the structure shift to higher energy with increasing sulphur concentration and disappears around x∿ 0.3-0.4. The same difficulty was previously reparted in absorption[8]. From our W.M.R. measurements, however, we associate the S_1 transition in GaSe with the pronounced doublet at 4.55 and 4.61 eV in GaS. The sudden change in transition energies at x 0.4 is probably due to the structural transition from ε-γ to β polytype in this composition range.

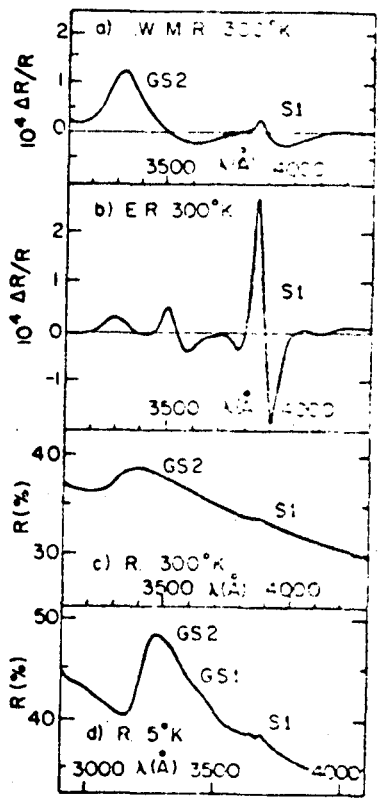

Fig.5. Several experimental spectra of the S_1 transition in GaSe.

Fig. 6 shows a plot of charge density contours and F_{xy} transition function for the S_1 transition. Both final and initial states have a strong Se character which explains the sensitivity of this transition to anion alloying and stacking effects. It is interesting to note that the direct gap belongs to this class of shift[5].

4. TRANSITIONS WITH MIXED ANION-CATION CHARACTER

Of course not all transitions exhibit the strongly typed Ga or S,Se character. Fig. 7 is a plot of 6 transitions varying with slopes between 300 and 400 meV. The indirect gap also belongs to this class of shift[5]. The precise walue of the shift depends on the relative amount of anion-cation hybridization for the wave function but the basic configuration of Ga bonding-antibonding charge density mixed with well localised S (Se) s and p charges remains constant for this class of transitions.

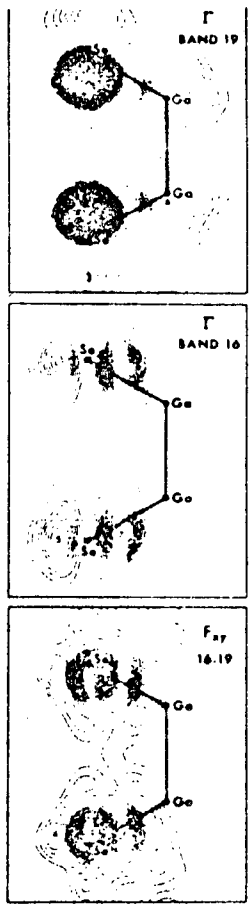

Fig.6. Charge density contours for the S_1 transition in GaSe.

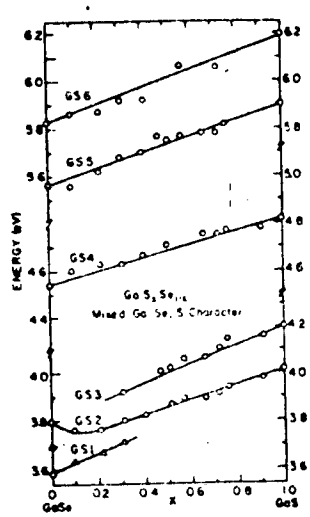

Fig.7. Energy diagram of the mixed anion-cation transitions in $GaS_x Se_{1-x}$.

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α Swiss National Science Foundation fellow.

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
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