

## Electron-energy-loss spectra of GaSe and Ga metal

Marisa Scrocco

*Istituto di Metodologie Avanzate Inorganiche del Consiglio Nazionale delle Ricerche  
and Istituto di Chimica Generale ed Inorganica, dell'Università degli Studi di Roma, I-00185 Roma, Italy*

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Measurements by electron-energy-loss spectroscopy allow us to differentiate surface from bulk phenomena at different incident energies  $E_p$ . It is also possible to highlight some peculiarities in GaSe crystal and in Ga metal. In particular, the characteristic Ga—Ga covalent bond present in GaSe is also evident in one of the bonds in Ga metal. The results are compared with previous experimental literature and discussed in terms of the band-structure calculations.

This paper presents electron-energy-loss spectra (EELS) of GaSe and Ga metal; two crystals that have very different structures and physical properties. GaSe is a III-VI layered compound with a trigonal prismatic structure in which the atoms are tightly bound in two-dimensionally extended layers (sandwiches).

Each layer (Fig. 1) has four close-packed monatomic sheets with a Se-Ga-Ga-Se arrangement; the interaction between adjacent layers (which is much weaker) is of the van der Waals type and explains the highly anisotropic mechanical properties of the crystal, which cleaves easily.

As for  $\text{PbI}_2$ , in GaSe the cations possess more electrons than are necessary to saturate the anion's valencies. In GaSe, this electron excess occupies an antibonding rather than a nonbonding band. Furthermore, in GaSe the bonding-band position differs from that of  $\text{PbI}_2$  because of the presence, in the gallium compounds, of a pair of neighboring cations (Ga—Ga) covalently bonded in the middle of each sandwich; this gives rise to a bonding-antibonding state.

The band-structure calculations of Schlüter<sup>1</sup> and Bourdon<sup>2</sup> establish that, in the case of GaSe, optical dipole transitions at the direct gap are allowed when  $E$ , the electric vector of the incident light, is parallel to the  $c$  axis (normal to the layer plane).

Measurements on Ga metal are included in this paper because they permit an interesting comparison with the Ga—Ga bond present in GaSe.

### EXPERIMENTAL PROCEDURE

The experiments were carried out in a high-vacuum (HV) apparatus [Vacuum Generators Ltd. model ESCA-3MK2 photoelectron spectrometer (VG ESCA-3MK2)] with a chamber equipped with an electron gun useful for Auger and energy-loss measurements. For GaSe, a single crystal was cleaved *ex situ* just before the experiment. The sample of Ga metal was prepared by evaporating *in situ* a Ga layer on a Cu plate in a  $1 \times 10^{-7}$  Torr vacuum. During all the measurements the vacuum in the apparatus was about  $1 \times 10^{-9}$  Torr.

Different incident energies were adopted in order to differentiate between surface and bulk phenomena, and

measurements at room and liquid-nitrogen temperatures were useful for recognizing the possible presence of excitons. The spectra were recorded with a modulation of 1.0 eV peak to peak and reported in second derivative because of its greater accuracy in the energy positions. The error limits are in the range  $\pm 0.3$ – $0.5$  eV.

### DISCUSSION

In the following discussion a brief mention of the GaSe structure can be useful to clarify the different

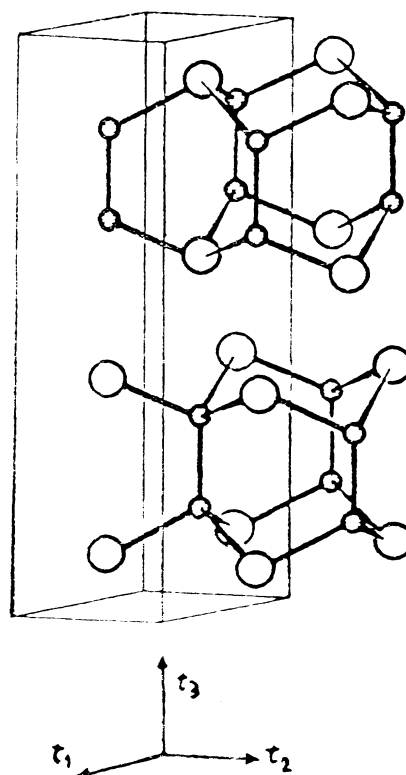


FIG. 1. Unit cell of  $\beta$ -GaSe. The Ga atoms are represented by small shared circles, the Se atoms by the large open circles. Reported from Schlüter (Ref. 1).

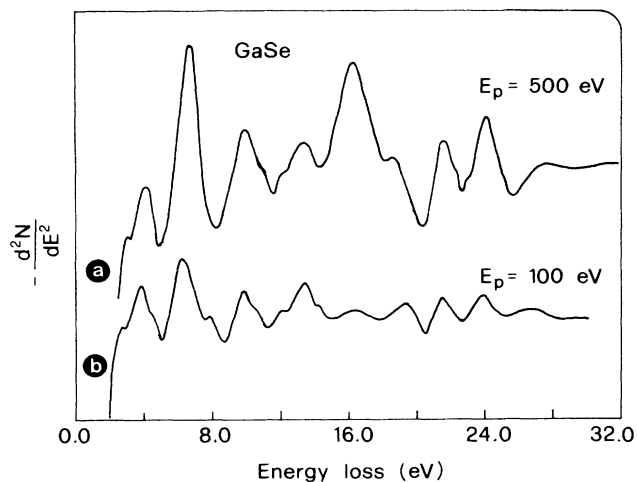


FIG. 2. EELS spectra of GaSe at  $E_p = 100$  and  $500$  eV.

properties of GaSe with respect to this compound. In GaAs, a semiconductor with the zinc-blende structure, the crystalline arrangement consists of two sublattices, one containing the anions (As) and the other the cations (Ga). Each anion in the crystal is surrounded by a tetrahedral arrangement of four cations and vice versa.

The occupied valence states are somewhat dominated by anion electrons: the lowest band being mainly  $s$ -like and the upper one being  $p$ -like. The analysis of the pseudopotential density profiles for GaAs (Ref. 3) shows a significant accumulation of charge within the neighborhood of the anion: The prolate ellipsoidal shape of the charge topography is characteristic of the hybrid  $sp^3$  orbital.

For the lowest conduction band, the pseudocharge density exhibits a charge localization around the anion site and suggests that the antibonding state is also partially anionic in character. Conversely, GaSe has a layered structure with strong characteristic anisotropy with

respect to one crystal axis and this drastically modifies the optical response. While the bonding between adjacent layers is of the van der Waals type, the bonds inside the layer are mainly covalent with some ionic character. Within a layer the atoms Ga and Se are not tetrahedrally coordinated as in GaAs, but each Ga is bound to three Se atoms and to another Ga atom; this cation-cation (Ga-Ga) covalent bridge represents the peculiarity of this structure.

The distribution at the valence levels in GaSe looks more complex than in GaAs (Ref. 4) because of the greater mixing between the  $4s$  and  $4p$  orbitals of both Ga and Se and the lower symmetry.

From the calculated energy levels of all the valence bands in the band-structure model<sup>1,5-7</sup> the authors concluded that two bonding-antibonding states connect the Ga—Ga covalent bond: (1) A bonding-antibonding state at the Ga  $4s$  levels originated by some hybridization with the Ga  $4p_z$  level: This antibonding state accommodates the excess of cation electrons present in the crystal. Because both these states are occupied, their weight in the cohesive energy is negligible. (2) A bonding-antibonding state at the valence level Ga  $4p$  generating the energy gap. In this latter case, the antibonding band is unoccupied and represents the first empty conduction band. In the proximity of the top of the valence band (between the Ga  $4s$  and the Ga  $4p$  levels) lie the anions  $4s$  and  $4p$  states which mix moderately with the cationic  $p_z$  orbital to form the top bond state of the gap.

*GaSe*: The electron-energy-loss spectrum of GaSe (Fig. 2) has a well-defined profile. A comparison between the spectra at  $E_p = 100$  and  $E_p = 500$  eV shows a strong enhancement of the peaks at  $6.4$  and  $16.0$ – $16.4$  eV at  $E_p = 500$  which establishes that they are bulk peaks.

The character of volume-plasmon loss of the  $16.0$ – $16.4$  eV peak is confirmed by Cazaux *et al.*<sup>8</sup> and Mamy *et al.*<sup>9</sup> Measurements at low temperatures (not reported in the figures) increase the resolution of the weak peaks.

Comparing our results with previous experimental works<sup>5,10-12</sup> and with the theoretical band structure and

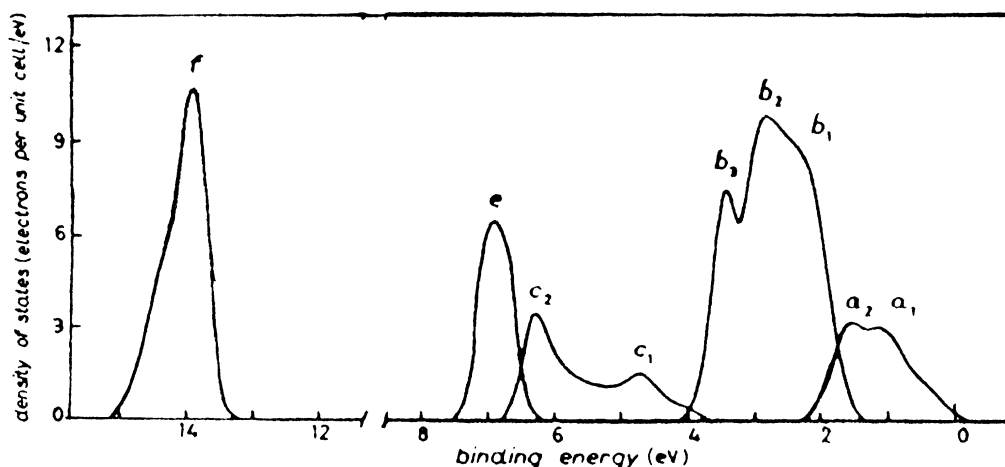


FIG. 3. Density-of-states functions of the single group of the valence bands of GaSe. Reported from Doni *et al.* [Ref. 13(b)].

the calculated density of states (DOS) of Doni *et al.*<sup>13</sup> (Fig. 3), it is possible to assign the peaks present in our EELS spectra. Care has to be taken in assigning the weak peaks present in these spectra as shoulders on the tails of the higher intensity peaks (particularly at  $E_p = 100$  eV), since they might be artifacts introduced by the second differentiation.

We are in no condition, with our experimental apparatus, to see the peak at 1.3 eV observed in the synchrotron-radiation photoelectron spectra by Magaritondo *et al.*<sup>10</sup> and by Thiry *et al.*<sup>11</sup> and attributed (because of its strong polarization sensitivity) to an essentially bonding Ga-Ga state formed by Ga  $p_z$  orbitals mixed with some nonbonding Se  $p_z$  orbitals.

Our peaks at 2.8–3.0 and 3.8–4.0 eV compare with Doni's peaks *b* (Fig. 3) and are attributed to Se  $p_x$  and  $p_y$  orbitals.<sup>1,13(b)</sup> In particular, the peak at 2.8 eV is interpreted as a transition associated with the excitation of the chalcogen  $p_x p_y$  electrons to the lowest conduction band.

Some discussion exists in the literature about the correct attribution of the peak at 3.8 eV. The suggestion of Piacentini *et al.*<sup>12</sup> is that this peak is associated with a transition between the highest valence band and the third group of conduction bands.

Our 6.4-eV peak (and the shoulder at 4.6 eV) compares with the *c* peaks and our 7.7-eV peak with the *e* peak of Doni *et al.*<sup>13(b)</sup> In the theoretical model, these last *c* and *e* peaks represent antibonding and bonding combinations, respectively, of the Ga 4*s* orbitals. Because of this correspondence, we attribute our peaks to transitions from these valence levels to the first empty states.

The peak at 13.5 eV is assigned to excitations from the Se 4*s* levels. Recently, Araki *et al.*<sup>14</sup> assigned this peak to a surface plasmon, but in our spectra, recorded at  $E_p = 100, 500,$  and 1000 eV, we do not find any variation in its intensity that could sensibly justify their attribu-

tion. Beside these peaks, we observe in our spectrum a doublet at 9.8–10.8 eV and a peak at 16.3 eV. This last peak is the bulk plasmon while the peak at 9.8 eV (the shoulder at 10.8 eV may be a spurious peak), observed also by Piacentini *et al.*, is assignable to an interband transition. The excitation of the Ga 3*d* level is present at 19.4 eV.

Other peaks present at  $\Delta\epsilon > 20$  eV, some of which were also observed by Cazaux *et al.*,<sup>8(b)</sup> are attributed to excitations from the Ga 3*d* levels. Indeed, also in our spectra they are large enough and asymmetric to suppose the presence of doublets due to the spin-orbit splitting (0.5 eV) of the *d* states as in Piacentini *et al.*<sup>12</sup>

We add Ga metal in this context because of the particular distribution of the atoms in its cell,<sup>15</sup> where every Ga has one very close nearest-neighbor atom at 2.44 Å and six other atoms further away at 2.71 and 2.79 Å. The close pair at 2.44 Å appears to form something like a molecule in the cell in the same way as the Ga-Ga covalent bond in GaSe and at the same distance.<sup>16</sup> This similarity suggests the presence of some covalent character in the bond of these two nearest-neighbor atoms: This suggestion appears to be supported by the energy gap occurring in the calculated band structure<sup>17,18</sup> just at the Fermi level around the  $\Gamma$ , *Z*, and *M* points in the Brillouin zone. These gaps which range over 1.25–2.45 eV, in a way, represent a measure of the covalency of this bond.

Indeed, in Fig. 4 and Table I, reporting the electron-energy-loss spectrum of Ga metal, a doublet is present at 6.4–7.3 eV very similar in energy to that observed in GaSe and attributed to the antibonding-bonding com-

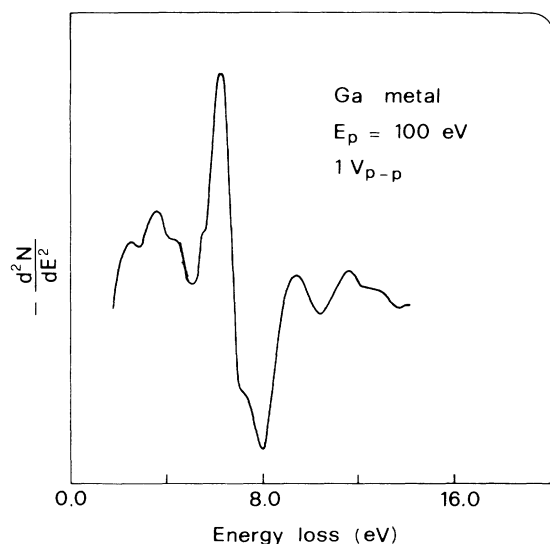


FIG. 4. EELS spectrum of Ga metal at  $E_p = 100$  eV.

TABLE I. GaSe and Ga metal peak positions ( $\Delta\epsilon$  in eV) below the elastic peak measured at incident-electron-beam energies of  $E_p = 100$  and 500 eV. The error limit is valued at  $\pm 0.3$ –0.5 eV. The peaks in parentheses may be extraneous peaks. See text.

GaSe		Ga metal	Assigned Ga metal transitions
$E_p = 100$ eV	$E_p = 500$ eV	$E_p = 100$ eV	
2.8	3.0	2.6	
3.8	4.0	3.6	$\Gamma_4 \rightarrow \Gamma_2$
(4.6)		4.4	$\Gamma_4^- \rightarrow \Gamma_4^-$
		5.6	
6.2	6.7	6.4	
(7.8)	(7.7)	7.3	
9.8	10.0	9.5	$Z_4^- \rightarrow Z_4^-$
(10.8)	(11.0)	11.6	$\Gamma_4^+ \rightarrow \Gamma_4^+$
12.2	12.2		
13.5	13.5		
(14.3)			
16.3	16.3		
	18.6		
19.5	(19.5)		
21.6	21.8		
23.8	24.1		

bination of the Ga 4s orbitals.

Between the energies corresponding to the gaps predicted in Hunderi and Ryberg's work,<sup>18</sup> our peak at 2.5 eV corresponds to their calculated transitions around the symmetry points  $\Gamma$  and  $Z$  in the Brillouin zone.

The other peaks at 3.6 and 4.4 eV are the interband  $\Gamma_4 \rightarrow \Gamma_2$  and  $\Gamma_4^- \rightarrow \Gamma_4^-$ ; the peak at 9.5 eV is assignable to  $Z_\mu^- \rightarrow Z_\mu^-$  and the peak at 11.6 eV to  $\Gamma_1^+ \rightarrow \Gamma_4^-$  as in our previous x-ray photoemission spectroscopy work.<sup>19</sup>

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