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Band structure of lead sulphide

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Abstract. The band structure of lead sulphide has been investigated using angle-resolved photoemission, with synchrotron radiation in the photon energy range 25–95 eV as the excitation source. Many spectral features originate from direct transitions, while others are due to 'density of state' features, i.e. they arise from electrons scattered into the observation direction. Good agreement was found between the experimental spectra and transitions expected on the basis of the calculated linearized muffin-tin-orbital (LMTO) band structure and free electron final states. Partial yield spectra at the Pb $O_{4,5}$ edge are also reported, from which it is concluded that the exciton energy in lead chalcogenides is not anomalously large, in contradiction to previous work.

1. Introduction

Lead sulphide is a narrow gap semiconductor belonging to the IV–VI family, and possessing rock salt structure. It was one of the first semiconductors to find wide application, where it served as the material for point contact diodes in so-called 'crystal set' radios. Present applications are limited to infrared detectors, while the IV–VI materials are generally candidates for long wavelength infrared lasers. Basic interest in these materials stems from their electronic properties and we report here a photoemission band mapping study supported by band structure calculations.

Although lead sulphide was one of the first solids to be studied thoroughly using angle-resolved photoemission with a resonance lamp (fixed photon energy) as the excitation source [1, 2], this early work has not been extensively followed up. Thiry *et al* [3] have published a very brief report of a synchrotron radiation study in which they compared their results with the calculations of Kohn *et al* [4]. Although a number of calculations have been performed over the years¶¶ none of these can be considered state-of-the-art.

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¶¶ See [4] and references therein.

2. Experimental details

Natural lead sulphide crystals from Broken Hill, Australia were used which were typically 3 mm × 3 mm × 7 mm; a semi-quantitative analysis is given in table 1. The samples were mounted by fixing them with epoxy resin to a metal substrate and then covering the epoxy with graphite. Analysis of the results after completion of the experimental work indicated emission for binding energies that did not relate to the known valence levels in the solid. It was therefore concluded that the sample had charged and that the spectra were shifted by 0.8 eV to a lower binding energy, relative to the valence band maximum. This effect was probably due to an inadequate sample contact, as the surface-photovoltage effect [5] is too small to account fully for the shift.

Table 1. Analysis of impurities in PbS.

Element	Concentration (ppm by weight)
Sb	650
Ag	225
Bi	140
Zn	<100
Sn	85
Cd	70

The samples were cleaved in ultra-high vacuum at a pressure of 2×10^{-9} mbar to reveal the (001) surface; Auger spectra showed no sign of elements other than lead and sulphur. A sharp (1×1) low energy electron diffraction pattern was observed, and no changes were noticed over several days, as expected from the very low reactivity of PbS [6].

Photons were obtained from beamline TGM 4 at the Berlin storage ring BESSY (Berliner Elektronenspeicherring für Synchrotronstrahlung GmbH). Photoemission spectra were measured with an angle-resolving spectrometer (ARIES from VSW Ltd), with the resolution set to 0.1 eV. Total resolution (photons + spectrometer) was better than 0.3 eV, corresponding to a momentum resolution of 0.01 \AA^{-1} at the highest kinetic energy.

All photoemission spectra were measured in normal emission with p-polarized light incident at 75° or 39° . Normal emission corresponds to the Γ -X direction in reciprocal space. The absorption spectra were measured by attaching a picoammeter to the sample and measuring total electron yield as a function of photon energy.

The photon energy was calibrated in the following manner. The electron energy analyser was calibrated against a digital voltmeter by observing photoemission spectra from the sample excited by a He discharge lamp, and then applying a voltage to the sample; the energy shift of spectral features was equal to the voltage applied to the sample, showing that the analyser was linear and precise. Synchrotron-radiation excited photoemission from the Pb 5d levels was then measured under conditions for which second-order radiation was present. The difference between the energy of the peaks is exactly equal to the energy of the first-order radiation. The photon energy range was 25 to 95 eV.

3. Computational details

The band structure was calculated via the linear muffin-tin-orbital (LMTO) method [7] using a Dirac relativistic version. The calculated band structure is shown in figure 1. The atomic sphere approximation (ASA) [8] was used, but the 'combined correcting term' was included, and ASA errors were minimized by inserting 'empty spheres' [9]. The local-density approximation was used with Perdew and Zunger's parametrization [10] of the Ceperley–Alder exchange–correlation potential [11]. On all sites, those with 'empty spheres' as well as those of real atoms, s, p and d partial waves were included.

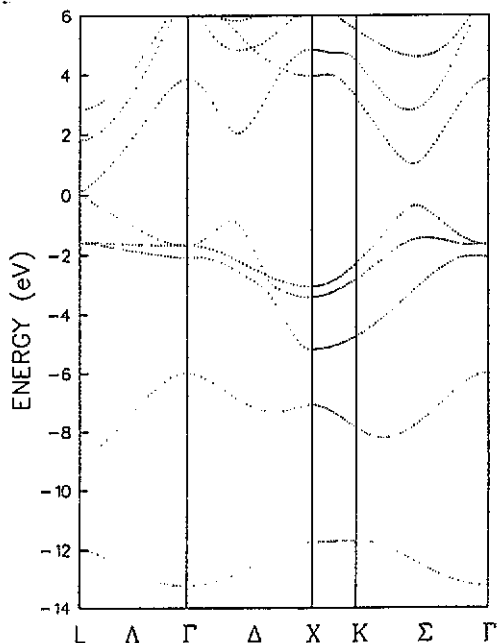


Figure 1. Calculated band structure of PbS along the high-symmetry directions. The zero of energy is the valence band maximum.

4. Results

4.1. Band structure

A selection of photoemission spectra is given in figure 2, showing several peaks with varying widths and peak forms. Some peaks disperse, while others are stationary and can therefore be assigned to either density-of-states effects or direct transitions from flat bands. A prominent example of the latter is the peak at 0.5 eV binding energy whose relative intensity changes, but whose binding energy is constant. Another noticeable feature is the strongly dispersing peak at about 12 eV binding energy. This originates from the sulphur 3s derived band, and is not observed for photon energies below about 40 eV due to low cross section.

Figure 3 shows a comparison of selected spectra at angles of 75° and 39°. For the first geometry, the major component of the vector potential A is normal to the surface. If the surface normal is denoted by z , then A_z is totally symmetric, and

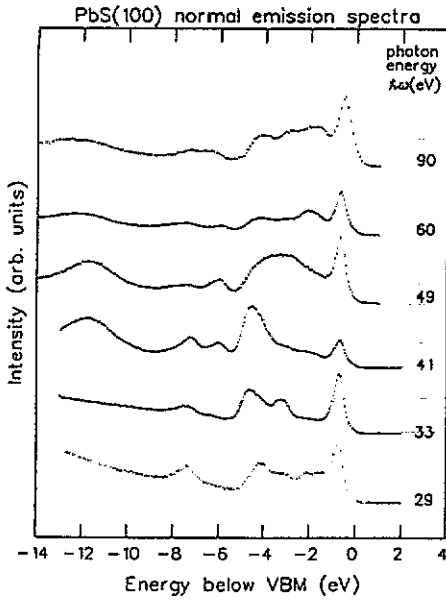


Figure 2. Normal-emission UPS spectra from PbS(100). The photon energies are given beside each curve. Light is incident at 75° along [010].

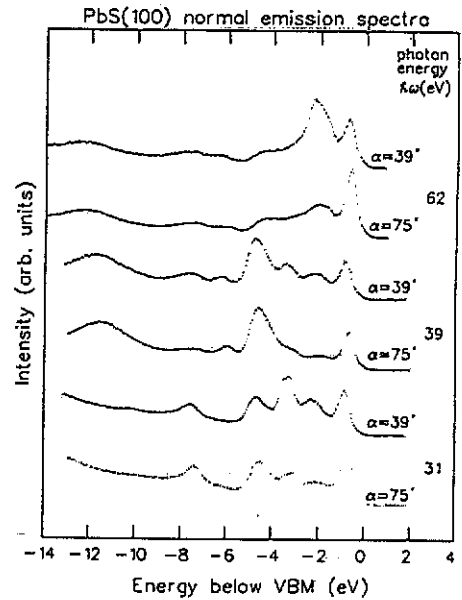


Figure 3. Comparison of photoemission spectra at angles of incidence $\alpha = 75^\circ$ and 39° at selected photon energies.

from the selection rules, totally symmetric states are favoured. Similarly, for a 39° angle of incidence, the antisymmetric component of the vector potential (parallel to the surface) is enhanced, and antisymmetric initial states are relatively more intense.

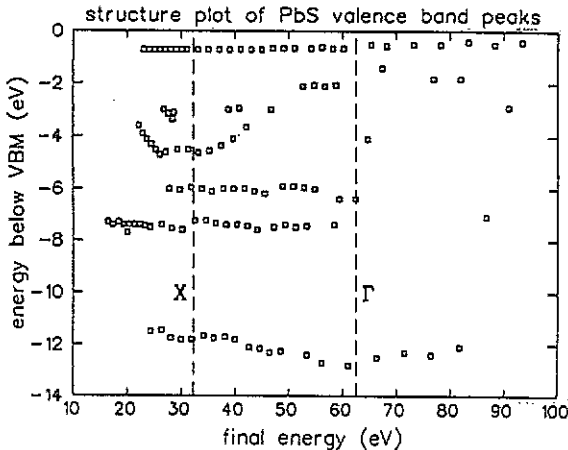


Figure 4. Structure plot of the binding energies of photoemission maxima against kinetic energy. Critical points are indicated.

The symmetry of the PbS(100) surface is C_{4v} , so we denote the symmetric states by Δ_1 . The antisymmetric states belong to the irreducible representation Δ_5 . Taking into account spin-orbit coupling, double group notation must be used, so that the symmetric states belong to the representation Δ_6 and the antisymmetric to Δ_7 .

The experimental results are summarized in a structure plot in figure 4. This is simply a plot of binding energy versus final-state energy and will be discussed further below.

4.2. Results: thermal effects

Thiry *et al* [3] reported strong temperature effects on the photoemission spectra of PbS. We investigated this as well, and the results are shown in figure 5. There is not a substantial difference between the spectra taken at 90 and 300 K: some peaks become sharper, and there are small changes in relative intensities, but the dramatic effects observed by Thiry *et al* were not observed.

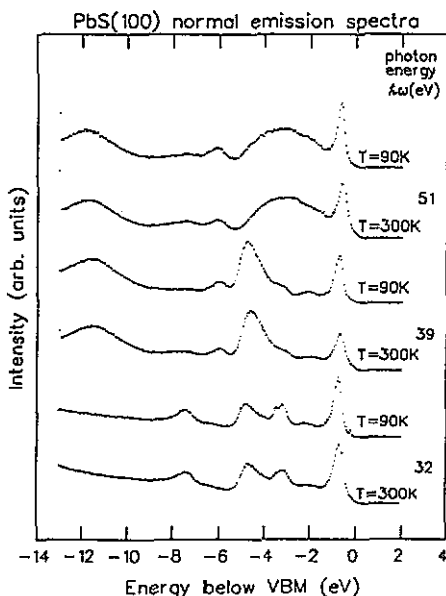


Figure 5. Thermal behaviour of photoemission spectra. Sample temperature and photon energy are given beside each curve.

In the present work we have used a more restricted range of temperature (90–300 K) than Thiry *et al* (20–300 K), but this does not seriously affect our conclusions. The most dramatic effects were observed by them between 300 and 100 K in their 72 eV spectrum (their figure 1). This is reasonable because, as they argue, differences are mainly expected above and below the Debye temperature (150 K).

At present we have no explanation for the fact that we observe much weaker effects than Thiry *et al*. Clearly more work is needed in this area.

4.3. Results: photoabsorption at the Pb 5d edges

Total yield absorption measurements at the Pb $5d_{5/2,3/2}(O_{4,5})$ edges were carried out by scanning the photon energy while measuring the photoelectric current from the sample. Results are shown in figure 6, together with the calculated density of unoccupied p-symmetry states.

Comparison of the two curves is complicated by three factors. Firstly the experimental curve contains two onsets, A and C. Secondly the intensity of the density-of-states features seems to decrease rapidly above the first threshold. Thirdly, the

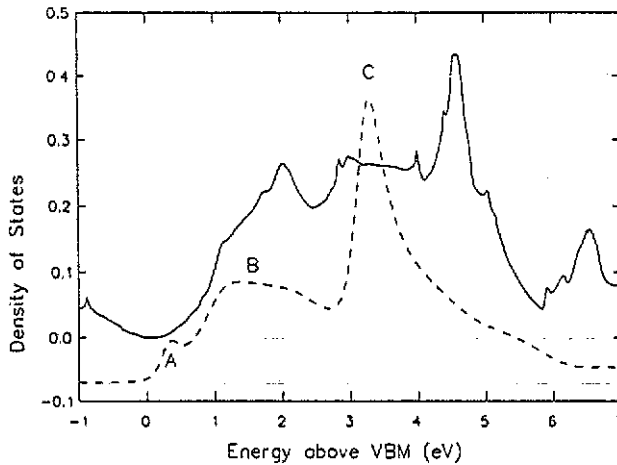


Figure 6. Dashed line: total secondary electron yield versus photon energy. Full line: theoretical density of p-symmetry states. For explanation, see text.

calculated density of states is l resolved and not j resolved (but spin-orbit coupling is included, of course). With these qualifications, the density of states does not show a step-like increase at threshold, but experimentally we do see a step, A. We identify this as either an exciton or an anomalous enhancement of the absorption strength at the threshold. The steep rise B is identified with the corresponding feature in the density of states, while the theoretical peak and valley at 1.8–2.2 eV seem to appear experimentally as a weak peak and a shifted valley. The peak C is identified with the onset of emission from the $5d_{3/2}$ level, and thereafter the absorption spectrum represents a mixture of features from both core levels.

We obtain an onset energy of 18.85 ± 0.1 eV. (In this case we used second- and third-order radiation for the calibration procedure described above.) We now wish to calculate the exciton energy, assuming that an exciton exists that is related to states at the bottom of the conduction band. To do this we need the binding energy of the Pb $5d_{5/2}$ level. Grandke and Cardona [6] obtained a value for the Pb $5d_{5/2}$ binding energy measured in photoemission of 18.87 ± 0.05 eV, independent of doping. They did not determine the position of the Fermi level within the gap, so we cannot calculate the binding energy relative to the conduction band minimum (CBM). However, if the Fermi level is pinned at the conduction band minimum, the exciton energy is 0.0 eV, and since the Fermi level must lie somewhere in the gap, the uncertainty is equal to the gap energy. Thus we can say that the onset energy is equal to the binding energy of the Pb $5d_{5/2}$ level to within an error equal to the gap energy (0.4 eV). We conclude that the exciton binding energy, which is the difference between the onset energy and the photoemission binding energy, which is the difference between the onset energy and the photoemission binding energy referred to the bottom of the conduction band, is between 0 and 0.4 eV (the gap energy); and if it is zero, then the onset corresponds to transitions to the bottom of the conduction band.

However, Martinez *et al* [12] have pointed out that, in the very similar cases of PbSe and PbTe, the bottom of the conduction band is composed of states having $6p_{1/2}$ character. From the selection rule $\Delta j = \pm 1, 0$, $5d_{5/2} \rightarrow 6p_{1/2}$ transitions are forbidden. They therefore argued that the onset represents transitions to the

Σ band, i.e. to the sixth band, at the minimum along the Σ line. Since this point lies about 0.9 eV above the bottom of the conduction band, they concluded that the exciton binding energy lies between 0.9 eV and 1.3 eV (0.9 eV plus the gap energy). It is, however, extremely unlikely that the exciton binding energy is two or three times larger than the gap energy and we therefore offer the following alternative explanation.

The interpretation of Martinez *et al* [12] assumes atomic-like orbital character, which is in fact an approximation since we are dealing with bands here. Theoretical analysis of the character of the empty bands indicates that the minimum at the L point is indeed dominated by Pb $p_{1/2}$ states, but this is not the sole contribution. The analysis is somewhat complex because the LDA approach is not very accurate near the gap. The general procedure is to analyse the character along the band in question at some distance from the L point and to extrapolate back: this avoids spurious effects such as inversion of the CBM and VBM. In this way it was found that the ratio of Pb $6p_{1/2}$ to Pb $6p_{3/2}$ character was about nine. This value is qualitatively consistent with the spectrum if we assign the first peak, A, to transitions from $5d_{5/2}$ to the minimum at L and the large peak, C, to transitions from $5d_{3/2}$ to the same point.

Another point is that relativistic optical selection rules may apply. The Pb $5d_{5/2}$ level belongs to the irreducible representation L_3 (at the L point) in single group notation, and $L_6^+ + L_{4,5}^+$ in double group notation [13]. The conduction band minimum at the L point contains mainly $6p_{1/2}$ states and belongs to the double group representation L_6^- . Borstel *et al* [13] have published the relativistic optical selection rules for this case: $L_6^+ \rightarrow L_6^-$ and $L_{4,5}^+ \rightarrow L_6^-$ transitions are allowed for light parallel and perpendicular to Γ -L respectively. Thus the onset corresponds to transitions to the bottom of the conduction band, and the exciton energy is between 0 and 0.4 eV, a much more reasonable value.

We are unable to say whether this case is dominated by band effects (admixture of $p_{3/2}$ states) or by selection rules, but in any case the message is clear: there is no abnormally large exciton energy in this system. This conclusion implies that the interpretation of the reflectivity data of Martinez *et al* [12] must be revised.

5. Evaluation and discussion

For the evaluation of the band structure data we follow a procedure similar to that of Hinkel *et al* [7]. The high-symmetry points Γ and X can be approximately located in the structure plot, figure 4, by calculating the momentum of the photoelectrons using an estimated value of the inner potential. At the symmetry points the bands show extremal behaviour, i.e. a maximum or minimum. From the exact location of this turning point, the inner potential can be calculated using a fitting procedure. We obtain a value of -8.45 eV, similar to the values obtained for PbSe (-7.2 eV) and PbTe (-8.0 eV) [7]. Thiry *et al* [3] found a value of -8.0 eV for PbS. With this inner potential, we obtain the plot of binding energy versus wave vector shown in figure 7.

Using this information, we can then plot the experimental band structure: figure 8. At a binding energy of 0.5 eV, there is a flat band whose binding energy is constant to within ± 0.1 eV. We interpret this as corresponding to a feature in the calculated density-of-states feature originating from the maximum at 0.8 eV about midway along Γ K (see figure 1). Photoelectrons originating from transitions from this point may be scattered into the normal emission direction and cause this peak.

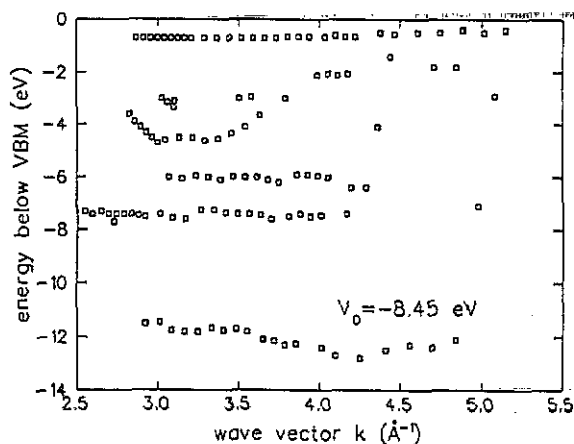


Figure 7. Photoemission binding energy versus wave vector, assuming a free-electron-like final state.

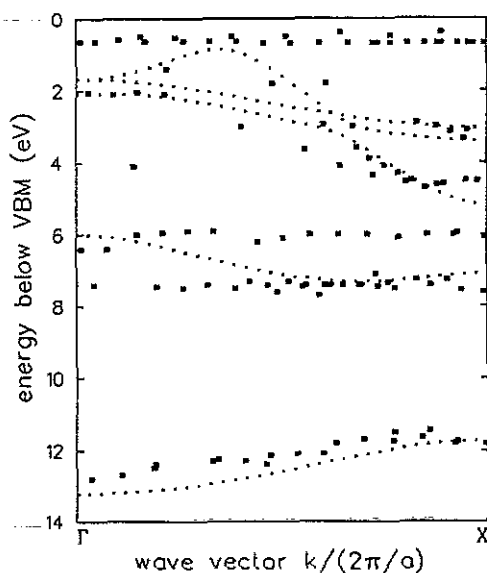


Figure 8. Experimental band structure (squares) and theoretical band structure (points).

From this peak to 4.7 eV, we see the sulphur derived p-bands which are predicted to lie between 0.9 and 5.2 eV. Experimentally we therefore have a band width which is about 0.5 eV smaller than predicted. The Pb 6s derived band is observed at 5.85–7.6 eV, and appears as two flat bands rather than as a single dispersing band. The band width of 1.75 eV is larger than the 1.35 eV predicted by theory. Also, the experimental dispersion is not in the expected direction, as a weak minimum is observed at Γ , where a maximum should be. We interpret these results as density-of-states features originating from states at Γ and the minimum along the line ΓX .

Finally, the 3s derived band is observed at 11.4–12.7 eV, i.e. at a slightly lower binding energy than predicted by theory. Again the band width is smaller than predicted by about half an electron volt. The dispersion of this band is in agreement with theory in that the minimum is at Γ . Experimentally the maximum occurs on the

Δ line, not at X, but near it, whereas theoretically it should be at X.

The present results may be compared with those of Thiry *et al* [3] who also studied PbS. They obtained very poor agreement with theory, partly because their theoretical description was rather poor. Some of their experimental features resemble our data qualitatively. For instance, they observe flat bands at the top of the valence band and in the region of the Pb 6s band. However, in general there are large differences: there are no data near X in the upper valence region or from the S 3s derived band (band 2, Δ_6), and the structure at Γ is different.

As stated previously, Hinkel *et al* [7] have studied the closely related compounds PbSe and PbTe. They obtained even better agreement with theory, partly because they also obtained data at low photon energy (< 25 eV), this being particularly useful for plotting the bands at lowest binding energy along ΓX . The assumption of a free-electron-like final state in this energy range seems to work particularly well for the lead chalcogenides, although as Hinkel *et al* pointed out, this was not expected. The deviations from theory are similar to the present case: the total width of the upper three bands is slightly less than predicted; the S 3s derived band has a slightly lower band width and binding energy than predicted and the Pb 6s band is at slightly higher binding energy than the theoretical value. We appear to have more density-of-states features than Hinkel *et al* but this is only apparent: in their band structure plots figures 6 and 7 they have omitted flat bands which are evident in their spectra, figures 1 to 4. We therefore conclude as they did that the observed spectra can be interpreted in terms of a mixture of flat bands due to density-of-state features and direct transitions.

The symmetry of the initial states was determined qualitatively by comparing spectra at 75° and 39° angles of incidence (figure 3). Peaks which were stronger for the first geometry (enhanced component of the vector potential perpendicular to the surface) are symmetric, while those stronger at $\alpha = 39^\circ$ (vector potential parallel to the surface enhanced) are antisymmetric, for non-relativistic selection rules and single group representations. The most pronounced effects occur in the 5 p-bands at 2 to 3.5 eV where the antisymmetric bands are clearly enhanced at a 39° angle of incidence. We have not attempted a quantitative evaluation for two reasons. Firstly, it is difficult to evaluate the experimental intensity because background subtraction and deconvolution are difficult. Secondly, the theoretical calculation is rather complicated as the dielectric constants and Fresnel equations at each energy must be considered [14]. Therefore, only qualitative conclusions are drawn. For direct transitions, the symmetry is in agreement with that predicted by theory. The indirect transitions (density-of-states features) also show some weak dependence on polarization.

6. Conclusions

We have mapped the band structure of PbS along $\Gamma-X$ and have obtained satisfactory agreement with LMTO calculations. The photoemission spectra show both direct and indirect transitions (or density-of-states features).

Total yield spectra at the 5d edges were used to determine the p-symmetry density of conduction states. We interpret the results in terms of relativistic selection rules and conclude that the excitonic binding energy is not more than the band gap (0.4 eV). This is in contradiction to previous reflectivity measurements on PbSe and PbTe.

A comparison of spectra at 90 and 300 K indicates that thermal effects are minor in this temperature range, from 0.6 to 2 times the Debye temperature.

Acknowledgments

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