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Spectroscopy of Acceptor States in ZnSe

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Introduction

ZnSe is of growing technological interest for applications as diverse as blue LEDs and THz emitters. Yet even fundamental data concerning acceptor states, such as the Luttinger parameters that characterise the valence band, remain controversial. We report the infrared absorption spectroscopy of ZnSe. Our data resolves features more clearly than does previous work. We discuss earlier interpretations of the myriad absorption features in light of our recent spectra and present a new explanation of the absorption associated with acceptor states.

Experiment

The sample used was a nominally undoped bulk crystal of ZnSe prepared by the solid-growth method, expected to contain Li as the chief unintentional impurity. The sample was wedged to suppress interference fringes. Measurements were made using a Bruker 113v Fourier spectrometer and a liquid-helium-cooled Si bolometer detector. The spectrometer resolution employed was 0.5 cm^{-1} or 0.06 meV ; the linewidths of donor lines have previously been determined to be $\sim 0.12\text{ meV}$, and the linewidths of acceptor lines to be $\sim 0.5\text{ meV}$.

Results and discussion

In none of our spectra did we observe infrared absorption due to donors, for example, the $1s \rightarrow 2p$ transition, which is known to lie at 19, 20, 21 and 22 meV for Al, Cl, Ga and In donors, respectively. This demonstrates the sample is *p*-type. Our spectra confirm in detail the absorption features reported previously for similar samples [1–4]. Higher resolution and better signal-to-noise in our experimental arrangement has allowed us to (1) resolve the “ $3S_{3/2}$ ” line, which formerly appeared as a shoulder; (2) discern new features in the region 118–125 meV ($950\text{--}1010\text{ cm}^{-1}$). Earlier determinations of transition energies for acceptor impurities in ZnSe have been made by photoluminescence (PL). These are given in Table 1 and compared with our data in Fig. 1. The acceptors for which PL data exists are N_{V1} , Li_{II} , As_{VI} and Na_{II} . The states are labelled according to the conventional notation based on atomic orbitals. The bracketed term following the atomic label is based on the symmetry of the state. This term alone is sufficient to unambiguously identify the state. In comparing our data with the PL, it is

Table 1: Experimental energies for transitions from the $1S_{3/2}(1\Gamma_8^+)$ ground state to some excited states in ZnSe for several shallow acceptor impurities, as determined by photoluminescence. The binding energy of the ground state (i.e. the ionization energy) is also given. Units are meV.

Final State	N [5]	N [6]	Li [7]	As [8]	Na [7]
$2P_{3/2}(1\Gamma_8^-)$	67.8	67.7 ± 0.2	72.9 ± 1	73.6	83.1 ± 1
$2S_{3/2}(2\Gamma_8^+)$	79.9	79.6 ± 0.2	82.6 ± 1	83.9	97.6 ± 1
$2P_{5/2}(2\Gamma_8^-)$	82.6	82.6 ± 0.2	85.8 ± 2		100.4 ± 2
$2P_{5/2}(1\Gamma_7^-)$	89.8	90.1 ± 0.2 (State $2P_{3/2}$)	93.0 ± 1	93.5	106.8 ± 1
$3S_{3/2}(3\Gamma_8^+)$	92.8		97.8 ± 1	98.4	110.5 ± 1
$2P_{1/2}(3\Gamma_8^+)$	98.5		100.0 ± 1		113.0 ± 1
$4S_{3/2}(4\Gamma_8^+)$	102.2		102.5 ± 1		114.7 ± 1
$5S_{3/2}(5\Gamma_8^+)$	103.4				
$6S_{3/2}(6\Gamma_8^+)$	105.0				
E_A	110	110	114	114.8	128

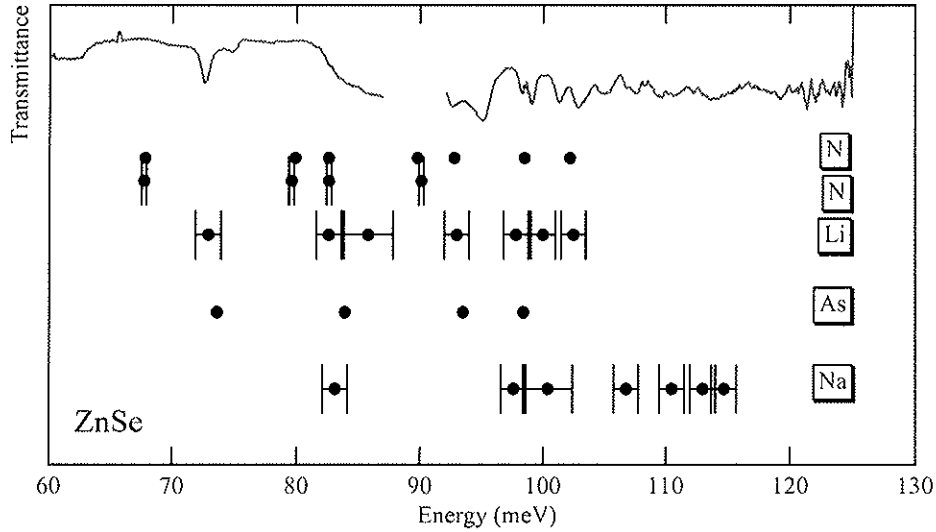


Figure 1: Experimental absorption spectrum at 4.2 K compared with transition energies as reported by PL. Note, the region around 90 meV is not accessible by our technique. The data for N, N, Li, As and Na acceptors are taken from references [5], [6], [7], [8] and [7], respectively.

vital to recognise that absorption spectroscopy is sensitive to odd-parity final states, whereas PL is sensitive to even-parity final states. We have closely examined the PL spectra and find many of the putative transitions to odd-parity states extremely weak. On the other hand, we do not expect to detect transitions to even-parity states in our data. The strong line at ~ 72 meV corresponds to the transition $1\Gamma_8^+ \rightarrow 1\Gamma_8^-$ observed in PL for either Li or As acceptor. We see no features that could relate to this transition for N or Na impurities. We do not see the $\rightarrow 2\Gamma_8^+$ transition (nor do we expect to) for any of these species. To compute the theoretical energy levels [9] requires the Luttinger parameters of ZnSe. Many sets of these have been published; some examples are given in Table 2. The energies of transitions calculated from these Luttinger parameters are compared with the experimental spectrum in Fig. 2, where all the (generic acceptor) calculations have been tied to the $\rightarrow 1\Gamma_8^-$ transition to take account of the central-cell correction, which is not part of the effective-mass approximation. It is seen that

Table 2: Luttinger parameters of ZnSe.

Source	γ_1	γ_2	γ_3
Lawaetz 1971 [10]	3.77	1.24	1.67
Sondergeld and Stafford 1975 [11]	3.23	0.69	0.90
Sondergeld 1977 [12]	3.13	0.694	0.902
Feierabend and Weber 1978 [13]	4.32 ± 0.20	0.662 ± 0.013	1.13 ± 0.02
Vengaus 1978 [14]	2.71 ± 0.60	0.63 ± 0.09	0.97 ± 0.21
Vengaus 1979 [renormalized] [15]	4.3 ± 0.5	0.59 ± 0.07	1.34 ± 0.30
Vengaus 1979 [bare] [15]	4.8 ± 0.6	0.67 ± 0.08	1.53 ± 0.35
Sermage and Fishman 1981 [16]	4.30	1.14	1.84
Oka and Cardona 1981 [17]	4.00	0.83	1.30
Hölscher <i>et al.</i> 1985 [18]	2.45	0.61	1.11
Mayer <i>et al.</i> 1995 [6]	(4.3)	1.04	2.00
Nakata <i>et al.</i> 1999 [2]	6.44	2.58	2.74
Dietl <i>et al.</i> 2001 [19]	2.95	0.6	1.11

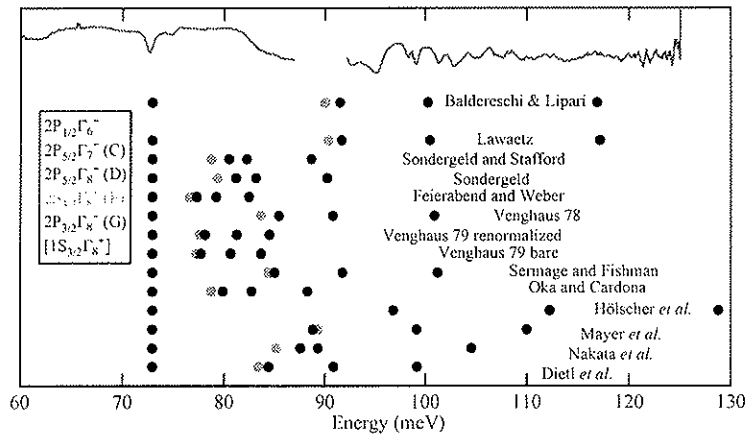


Figure 2: Experimental spectrum compared with theoretical transition energies calculated using various sets of Luttinger parameters. Red are even-, black are odd-parity final states.

some sets of Luttinger parameters are inconsistent with our data, predicting transitions to additional odd-parity states below 85 meV that we do not observe. On the basis of our data and this analysis we conclude the Luttinger parameters of Refs. [6], [10] and [18] are the most reliable. Many more lines are evident in our spectrum than in either the PL data or the theory for a simple acceptor. The multiplicity of lines has been successively attributed to (a) phonon replicas [2], (b) simultaneous excitation of donors [3] and (c) splitting of the states due to the off-site location of the Li ion [4], as illustrated in Fig. 3. The assignment as phonon replicas is questionable in so far as the “replicas” are sometimes narrower than the parent lines, the splitting of states not fully convincing in that only selected transitions appear for a given state.

Conclusion

On the basis of the data and analysis presented we conclude that the origin of the complex structure in the absorption spectrum of ZnSe is the presence of *two* acceptors, Li and As.

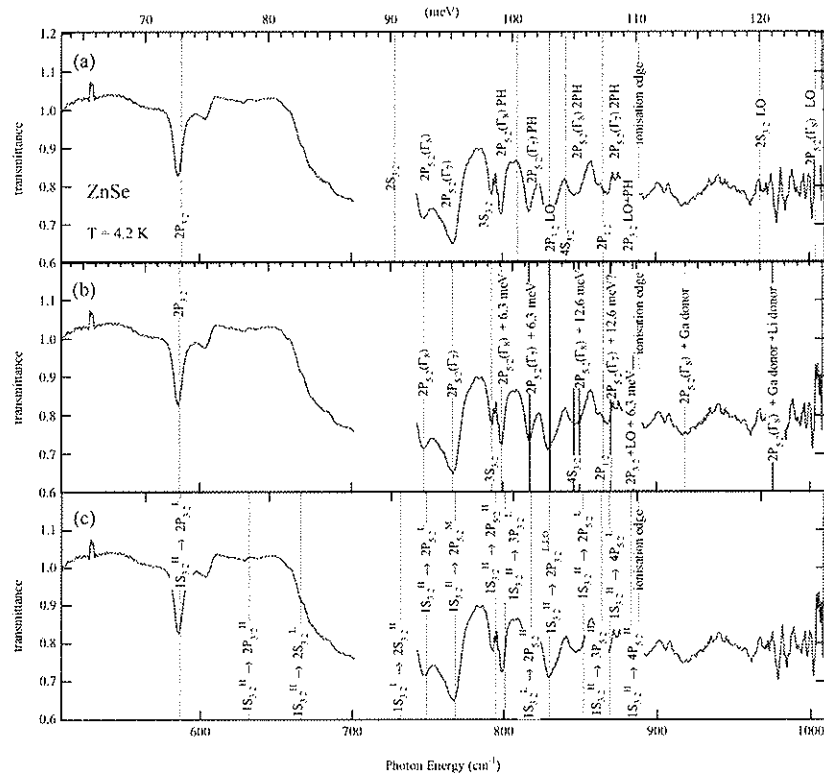


Figure 3: Interpreting structure of ZnSe spectrum in terms of (a) phonon replicas [2], (b) donor excitation [3] and (c) splitting of states due to acceptor displacement [4].

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