COMMENTS AND ADDENDA

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Donor-acceptor pair lines in ZnSe: An addendum

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Previously unidentified close pair lines are reported, and the energies of all pair lines observed in ZnSe are given.

Recently, there has been renewed theoretical interest in the luminescence from donor-acceptor pair recombination processes in compound semiconductors.[1–12] Although this phenomenon has been well understood in broad terms for over 10 years,[13] discrepancies exist between the theoretically calculated energies of discrete pair lines and the observed spectra.[1–5] Other problems, such as the fine-structure splittings of individual pair lines,[6–9] the minimum pair separation for binding an electron and hole,[10,11] and the dependence of the peak energy of the distant pair band on excitation intensity,[12] are presently being considered. There exists in the literature an abundance of experimental information concerning pair recombination in III-V and II-IV compounds; a comprehensive review has recently been published.[14] However, the experimental results are usually reported with insufficient detail to facilitate theoretical calculations. For example, the energies of discrete pair lines are usually plotted as a function of lattice separation with much less energy resolution than the data permit.

Donor-acceptor pair luminescence in ZnSe has recently been described by Merz, Nassau, and Shiever (MNS).[15] Three type-I (Ref. 16) pair systems were observed involving the previously identified[17] shallow donors Al, Ga, and In, and the Li acceptor. Another pair spectrum had earlier been reported[18] which is also type I, but which shows an unexplained doubling of all lines; this system, referred to as the DM pair spectrum, remains chemically unidentified.[15] It is the purpose of this brief addendum to the work of MNS (i) to report previously unidentified close pairs in the pair spectra of ZnSe, (ii) to comment on other unobserved close pairs and, (iii) to list the energies of the pair lines to within the accuracy of the experiments.

The energies of all observed ZnSe pair lines are given in Table I. These energies have been measured from photographic plates by a least-squares fit to a Fe calibration spectrum; experimental details are given by MNS. This fitting procedure is accurate to 0.02 meV; however, because of the width of the pair lines, their energies are accurate to 0.05 meV. Distant pairs have been identified to shell numbers as large as 125 (donor-acceptor pair separation of ~45 Å),[16] although fine structure can be resolved only for close pairs.

Calculations of the minimum donor-acceptor pair separation for binding an exciton have recently been reported by Munschy and Stebe.[10,11] For comparison with experiment, it is important to determine the separation of the closest pairs actually observable. In ZnSe, it is difficult to observe pairs closer than shell $m = 10$, because of intense bound exciton lines at higher energies. MNS have reported $m = 10$ lines for the Al-Li, Ga-Li, and DM pairs. In the case of In-Li pairs, the $m = 10$ lines is masked by the I_1^{DEEP} line, which is believed to result from the recombination of an exciton to a neutral (but chemically unidentified) acceptor.[15] At higher energies, nominally undoped ZnSe crystals show a "window" in the spectrum between I_1^{DEEP} at 2.7827 eV and I_1^X at 2.7920 (Ref. 17) (believed to be the neutral Li acceptor bound exciton line[15]).

TABLE I. ZnSe pair-line energies. The accuracy of the reported energies is ± 0.00005 eV. Lines marked I are obscured by bound-exciton lines or their phonon replicas.

		Energy (eV)				
Shell No.	r (Å)[a]	Al-Li	Ga-Li	In-Li	DM pairs	
9	12.03	2.786 92	2.786 13	2.785 86	2.787 34	2.787 00
		655	571	550	671	...[b]
		613	534	513	655	...[b]
10	12.68	387	327	I	424	391
11	13.30	081	013	2.779 71	I	I
		036	2.779 26	895	I	I
12	13.89	2.778 90	784	746	...	2.779 16
		815	712	677	...	839
13	14.46	700	608	575	2.777 70	738
		647	545	498	706	681
		607	496	457	656	630
15	15.53	267	153	109	324	291
		227	114	070	291	259
16	16.04	...	2.769 14	2.768 61	085	058
17	16.53	2.768 64	746	692	2.769 23	2.768 95
		819	698	...	...	...
		784	668	622	844	816
18	17.01	698	580	519	763	734
		...	548	...	...	...
		630	512	460	692	662
19	17.48	600	473	423	...	629
		579	452	399	629	607
		552	426	366	607	584
		515	366	309	548	518
20	17.93	415	286	232	474	443
21	18.37	242	119	I	304	272
		206	I	I	272	241
22	18.81	I	I	2.759 34	194	158
		I	I	901	158	121
23	19.23	I	2.758 57	791	I	I
		I	828	762	I	I
24	19.64	2.758 59	709	653	I	I
25	20.05	780	647	585	2.758 45	2.758 06
		734	600	...	...	...
		719	585	523	806	765
		672	538	477	735	701
26	20.44	608	473	404	672	641
27	20.83	...	403	331	601	576
		514	380	313	576	550
		476	328	263	534	500
28	21.26	381	270	199	476	446
		331	228	160	433	399
29	21.59	271	169	I	376	344
31	22.32	I	2.749 81	2.749 11	159	126
		086	952	885	I	I
33	23.03	2.749 54	829	756	013	2.749 79
		936	800	...	...	...
		922	783	717	2.749 79	956
34	23.38	882	738	684	...	927
		858	727	668	...	919
		826	666	634	...	846
35	23.72	730	633	596	815	801
		694	591	552	801	764
36	24.06	633	546	511	...	...
37	24.39	592	483	405	...	660
		549	448	370	660	626
38	24.71	520	405	319	...	590
		482	372	301	590	555
39	25.04	452	337	255	...	521
		412	310	233	521	489

TABLE I. (*Continued*).

Shell No.	r (Å)[a]	Energy (eV) Al–Li	Ga–Li	In–Li	DM pairs	
40	25.36	2.743 78	2.742 65	2.741 87	···	2.744 52
41	25.67	339	220	145	···	397
		···	···	124	2.743 97	365
		316	184	106	365	···
42	25.98	293	145	060	···	335
		269	118	043	335	···
43	26.29	220	078	011	306	···
		···	···	2.739 88	···	242
44	26.59	···	···	927	···	183
45	26.90	103	2.739 56	871	141	109
47	27.49	2.739 90	848	762	···	064
		···	···	740	064	035
49	28.07	886	734	645	2.739 58	2.739 29
50	28.35	855	716	592	···	903
51	28.63	···	650	···	···	868
52	28.91	720	592	498	···	···
53	29.19	684	531	448	762	724
55	29.73	604	451	358	686	645
57	30.27	513	357	268	590	552
58	30.53	···	321	···	···	519
59	30.80	424	273	185	···	469
60	31.06	···	···	141	···	434
61	31.31	360	179	105	400	374
63	31.82	281	120	039	2.733 16[c]	
65	32.32	202	052	2.729 60	280	
		184	···	···	243	
67	32.82	130	2.729 80	915	···	
		···	···	889	179	
69	33.30	072	913	829	118	
70	33.54	···	···	789	···	
71	33.78	···	835	747	···	
72	34.02	···	···	···	023	
73	34.25	2.729 36	783	694	2.729 77	
75	34.72	881	727	630	920	
76	34.95	···	691	···	878	
77	35.18	836	661	584	851	
79	35.64	781	606	517	807	
81	36.08	726	551	462	749	
83	36.53	670	503	413	706	
85	36.96	614	461	368	654	
87	37.40	565	405	320	606	
89	37.82	···	355	274	559	
91	38.25	482	315	227	518	
93	38.66	424	···	185	476	
95	39.08	···	···	···	431	
97	39.49	352	191	097	396	
103	40.69	236	073	2.719 84		
106	41.28	···	···	933		
109	41.86	···	···	874		
111	42.24	090	2.719 34	842		
115	42.99	033	866	782		
117	43.37	2.719 94	838	746		
119	43.74	···	···	721		
125	44.82	···	···	653		

[a] Using zinc-blende ZnSe lattice constant $a_0 = 5.67$ Å.
[b] These lines appear as an unresolved band from 2.786 55 to ~2.7859 eV.
[c] The doubling of the DM pairs is not resolvable for $m > 61$.

TABLE II. Inequivalent sites and their degeneracies for shells 1–10 of type-I pairs. This information for shells 11–30 is given in Ref. 15.

Shell No.	r(Å)	Number of inequivalent sites	Degeneracies
1	4.01	1	12
2	5.67	1	6
3	6.94	2	12,12
4	8.02	1	12
5	8.97	1	24
6	9.82	2	4,4
7	10.61	2	24,24
8	11.34	1	6
9	12.03	3	12,12,12
10	12.68	1	24

However, when crystals are doped sufficiently to exhibit discrete pair lines, I_1^X becomes intense, and the "window" is closed by the acoustic phonon wing of I_1^X, making the observation of pair lines in this energy region extremely difficult. This can clearly be seen in the low-resolution pair spectrum [Fig. 1(a)] given by MNS. A careful search in this energy region has revealed the presence of a weak triplet corresponding to the $m=9$ pair lines, unreported by MNS. The energies of these lines are included in Table I. Other possible close pairs are listed in Table II. The $m=8$ singlet should be much weaker than observed pairs (degeneracy 6 instead of 12 or 24). Closer pairs ($m<8$) would occur where the I_1^X acoustic phonon is stronger, or where the I_2 and I_3 bound excitons dominate the spectrum.[17] For these reasons it is felt that, although pair recombination may in fact occur in ZnSe for pair separations less than 12 Å, bound exciton luminescence from these same donors and acceptors makes the observation of such pairs experimentally unlikely.

[1]L. Mehrkam and F. Williams, Phys. Rev. B 6, 3753 (1972).
[2]F. Williams, J. Luminescence 7, 35 (1973).
[3]R. Bindeman and K. Unger, Phys. Status Solidi B 56, 563 (1973).
[4]V. Schröder, Verhandlungen der Deutschen Physikalischen Gesellschaft, Münster, 1973 (unpublished).
[5]K. Kreher, Phys. Status Solidi B 56, K75 (1973).
[6]L. Patrick, Phys. Rev. 180, 794 (1969).
[7]T. N. Morgan and H. Maier, Phys. Rev. Lett. 27, 1200 (1971).
[8]E. I. Rashba, Fiz. Tverd. Tela 12, 2963 (1970) [Sov. Phys.-Solid State 12, 2391 (1971)].
[9]A. R. Hutson, Bull. Am. Phys. Soc. 18, 380 (1973).
[10]G. Munschy and B. Stebe, Phys. Status Solidi B 59, 525 (1973).
[11]B. Stebe and G. Munschy, Phys. Status Solidi B 60, 133 (1973).
[12]E. Zacks and A. Halperin, Phys. Rev. B 6, 3072 (1972).
[13]For example, cf. D. G. Thomas, M. Gershenzon, and F. A. Trumbore, Phys. Rev. 133, A269 (1964); D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. 140, A202 (1965). A more complete list of references is given by MNS (Ref. 15).
[14]P. J. Dean, *Progress in Solid State Chemistry*, edited by J. O. McCaldin and G. Somorjai (Pergamon, New York, 1973), Vol. 8, p. 1.
[15]J. L. Merz, K. Nassau, and J. W. Shiever, Phys. Rev B 8, 1444 (1973).
[16]For type-I pairs, the donor and acceptor are on the same sublattice. In this case, the shell number m and pair separation r are related by $r=(m/2)^{1/2}a_0$, where a_0 is the lattice constant.
[17]J. L. Merz, H. Kukimoto, K. Nassau, and J. W. Shiever, Phys. Rev. B 6, 545 (1972).
[18]P. J. Dean and J. L. Merz, Phys. Rev. 178, 1310 (1969).