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IV-3. Sharp Line Emission due to Preferential Pairing in ZnO Crystals

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Sharp line emission spectra due to alkali metal doping have been observed in ZnO crystals at ~1°K. These spectra have been interpreted in terms of bound exciton complexes involving donor acceptor pairs.

§ 1. Introduction

It has been pointed out by Halsted[1)] that emission spectra due to the preferential pairing of emission centers should be expected in the chalcogenides of Zn, Cd, and Hg. The coulomb attractive forces between donor and acceptor centers would naturally give rise to preferential pairing of such centers in the more ionic compounds. At the temperatures required for single crystal growth, atomic or defect diffusion is rapid and it is reasonable to expect that the electrostatic attraction between centers will lead to deviations from a random distribution of donor-acceptor pairs. The distribution would be expected to shift in favor of higher concentrations of near neighbor pairs.

A number of sharp spectral lines have been observed in the emission from ZnO single crystals[2)] that were grown from the vapor phase without intentional doping. Several of these lines occur in the spectral region of interest in the present paper, namely, between 3696.5 and 3687.6 Å. These lines have been previously interpreted[2)] as optical transitions, arising from the creation and annihilation of bound-exciton-complexes. These interpretations were based upon analyses of Zeeman patterns and splitting characteristics of the lines. The number of sharp emission lines in the above spectral region is noticeably increased when the ZnO crystals are doped with alkali metals. The additional sharp lines result from the doping and are grouped around four of the lines that are observed in the undoped crystals. These four lines, which are consistently observed in the undoped crystals, have been interpreted as transitions arising from excitons bound to either neutral donors or acceptors.

The undoped crystals have low resistivities which increase markedly with the addition of alkali metals. One interpretation for the increase in resistivity is that the alkali metal atoms go into the lattice as acceptor impurities; consequently, compensating centers are introduced. If these centers are paired with the centers responsible for the undoped emission lines, it is reasonable to conclude that the undoped lines result from excitons bound to neutral donor sites. The orientation dependence of the Zeeman splitting of some of the paired lines does not conform to the lattice symmetry of the host crystal. The lack of host lattice symmetry can be explained on the basis of the local symmetry of the pairs, in the case where their orientation in the host

Table I. Emission lines observed in ZnO : Li crystals.

	Wavelength (Å)		Line Strength
I	3696.56	*	
	3695.40	+	S
II	3692.67	*	
	3691.85	−	S
	3691.37	−	S
	3691.17	−	S
III	3689.53	+	S
	3689.31	+	S
	3689.06	*	W
	3688.87	−	W
	3688.63	+	W
	3688.39	*	S
	3688.13	+	S
	3687.83	+	S
	3687.66	−	S

S refers to a strong line and W to weak line
* lines in undoped crystal
\+ lines that occur only in Li doped crystals
− lines that occur in both Na and Li doped crystals
□ lines that occur only in Na doped crystals

lattice is a factor. The spacings and multiplicities of the lines indicate that only closely spaced pairs are involved in the spectra with which we are presently concerned.

§ 2. Experimental Results

The detailed experimental arrangement has been described elsewhere.[2] In undoped ZnO crystals, four fairly strong uv-excited emission lines appear at wavelengths of 3696.56, 3692.67, 3689.06 and 3688.39 Å; however, intentional doping with Li gives rise to additional sharp lines in the crystal spectra and these lines appear near the four original lines. The spectral positions of the undoped lines, as well as those that appear with Li doping, are indicated in Table I. For analytical purposes, the lines have been separated into three groups, as shown in the table. The Zeeman splittings of the group I lines are shown in Figs. 1(a) and 1(b). In Fig. 1(a), the splitting of the 3696.56 Å undoped line, as well as the splitting of the 3695.40 Å Li-doped line, is shown as a function of magnetic field strength up to 40000 G. The data

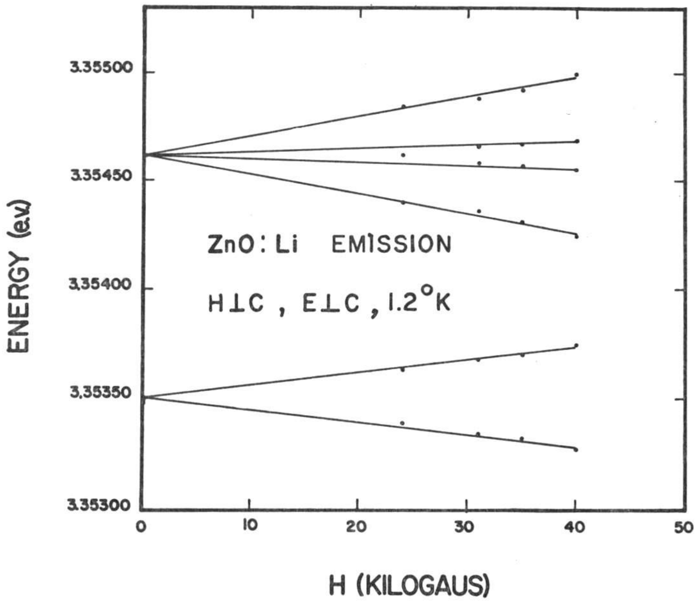

Fig. 1(a)

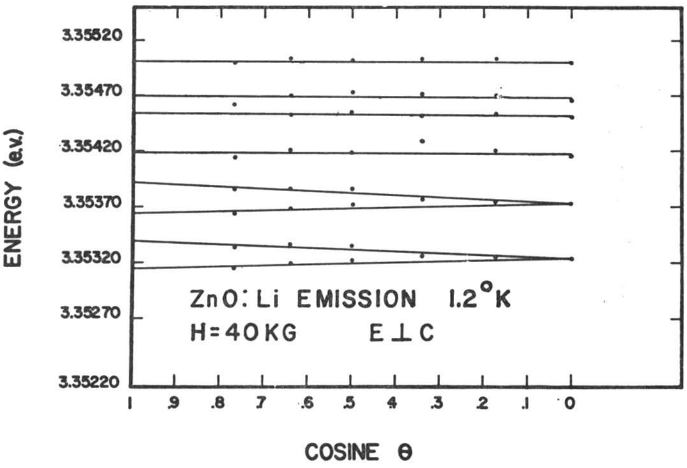

Fig. 1(b)

Fig. 1(a): Splitting of two ZnO emission lines as a function of magnetic field strength at 1.2°K. Fig. 1(b): Splitting of the two emission lines from Fig. 1(a) as a function of crystal orientation (cos θ).

is recorded for the crystalline *c*-axis oriented perpendicular to the direction of the magnetic field ($C \perp H$).

The undoped line splits into two components as is expected for a point substitutional impurity in the wurtzite lattice, where the point group symmetry is assumed to be C_{3v}.[4] The undoped line splits into two components, rather than four, as a consequence of the fact that the hole g-value goes to zero in the orientation, $C \perp H$.[3] On the other hand, it is interesting that the line which results from Li-doping (the quartet system of Fig. 1(a)) splits into four components for the $C \perp H$ orientation. This observation indicates a lowering of the point group symmetry of the impurity, so that symmetry considerations no longer require that the hole g-value be equal to zero at $C \perp H$. In Fig. 1(b), we see the solid-emission-spectrum analog to the classical Zeeman effect of atomic spectra. Here we have plotted the splittings of both the 3696.56 and 3695.40 Å lines as a function of $\cos\theta$ for a constant magnetic field strength of 40000 G; θ is the angle between the crystalline *c*-axis and the direction of the magnetic field. Of particular interest is the splitting of the 3696.56 Å line (the undoped line or lower-energy quartet). This line splits into four components for any arbitrary orientation of the crystal in the field, *i.e.*, for $0° < \theta < 90°$. When the crystal is rotated to the $C \parallel H$ position ($\theta = 0°$, $\cos\theta = 1$), the transitions involving the two outside components are spin-forbidden so that only two lines are observed when the crystal is oriented such that $\cos\theta = 1$; likewise, as shown above, only two components are observed when the crystal is oriented such that $\cos\theta = 0$. These observations are again what one would expect[3] for a substitutional impurity of point group symmetry C_{3v}. The Li-doped line shows an essentially isotropic splitting, as can be seen from the higher-energy quartet of Fig. 1(b). The hole and electron g-values can be calculated from the Zeeman splittings, using the relations,[2]

$$\Delta E = g\beta H \quad \text{and} \quad g = g_e \pm g_h = g_{eo} \pm g_{h\parallel} \cos\theta \,,$$

where β is the Bohr magneton; g_e and g_h are electron and hole g values, respectively; g_{eo} is the isotropic g-value of the electron; $g_{h\parallel}$ is the g-value of the hole when $C \parallel H$; and θ is, as usual, the angle between the *c*-axis and the direction of H. The electron g-value, known to be isotropic, has previously been determined[2] to be about 1.95 for all bound exciton lines in ZnO. The anisotropic hole g-value for the undoped line was calculated to be 1.01 ($C \parallel H$). A similar calculation for the Li-doped line gives an isotropic g-value of 0.74. In ZnO, the hole g-values are dependent upon the exact state of binding of the hole in the exciton complex; hence, the hole g-values not only vary from emission line to emission line, but are also anisotropic for a given line. However, as one can see from above, the Li-doped line does not give rise to an anisotropic hole g-value; this only means that the impurity which gives rise to this line does not have the C_{3v} point group symmetry of a substitutional impurity.

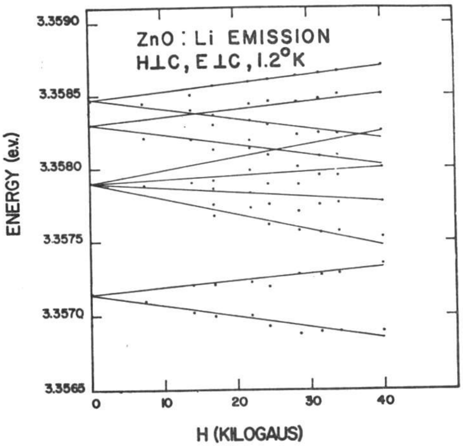

Fig. 2(a)

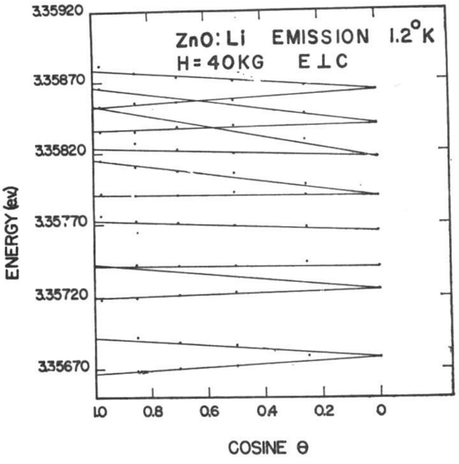

Fig. 2(b)

Fig. 2(a): Splitting of four ZnO emission lines as a function of magnetic field strength at 1.2°K.
Fig. 2(b): Splitting of the emission lines from Fig. 2(a) as a function of crystal orientation ($\cos\theta$).

In group II set of lines, the undoped line is the 3692.67 Å line. The additional lines in this group arise from the Li-doping and are shown in Table I. The Zeeman splittings of these lines are shown in Figs. 2(a) and 2(b). The splittings of the lines as a function of magnetic field strengths are shown in Fig. 2(a) for fields strengths up to 40000 G and a crystal orientation of $C \perp H$. Just as in the group I lines above, the undoped line splits into two components, as expected for the substitutional point symmetry of the wurtzite lattice. The next higher-energy line in Group II arises from the Li-doping and appears at a wavelength of 3691.85 Å; it splits into four components in a magnetic field for the orientation $C \perp H$. This splitting again indicates a lowering of the point group symmetry for the "doped" line; such a splitting might be explained on the basis of orientation of the pair in the lattice. The next two higher-energy lines (3691.37 and 3691.17 Å) result from the Li-doping and each splits into two components. As shown in Fig. 2(b), the splittings of all of the above lines are plotted as a function of $\cos\theta$ at a constant magnetic field strength of 40000 G. For the undoped line (3692.67 Å), the hole g-value was calculated to be 1.24. The calculated hole g-value for the "doped" line (3691.85 Å) is 1.12, with a very small angular dependence. The next two higher-energy lines split approximately the same as the "undoped" lines.

Table II. Emission lines observed in ZnO : Na crystals.

Wavelength (Å)			Line Strength
I	3696.56	*	
	3693.20	□	W
II	3692.64	*	
	3692.10	□	W
	3691.80	—	W
	3691.36	—	W
	3691.17	—	W
III	3689.65	□	S
	3689.26	□	W
	3689.03	*	S
	3688.77	—	S
	3688.47	□	W
	3688.19	□	S
	3687.90	□	W
	3687.62	—	S

The meaning of notations are the same as in Table I.

There is a greater multiplicity of lines in group III than in the other two groups. There are two "undoped" lines associated with the third group, namely the 3689.06 and 3688.39 Å lines. The multiplicity and close spacings of lines makes it very difficult to analyze the Zeeman patterns of the lines in this group. Even at low magnetic fields, line crossings often make it impossible to identify split components with their parent lines.

A similar set of experiments was done on crystals that were Na-doped rather than Li-doped. Several additional sharp lines again appeared in the same three spectral groups as was observed for the Li-doped crystals. These groups of lines are shown in Table II. For the same doping concentrations that were used in the Li-doped samples, it is interesting to note that there were small shifts in the spectral positions of the lines as well as difference in line intensities. It was also observed, in both Na and Li-doped samples, that as the concentration of the dopant increased the intensity of the "undoped" lines decreased while the intensity of the "doped" lines increased.

§ 3. Conclusion

The model that is adopted to explain the sharp line spectra of both doped and undoped ZnO crystals is that of the bound exciton complexes. The sharp line spectra from the undoped crystals are interpreted in terms of excitons bound to neutral donor sites. The Zeeman patterns of these lines are compatible with this interpretation. On the basis of resistivity measurements,

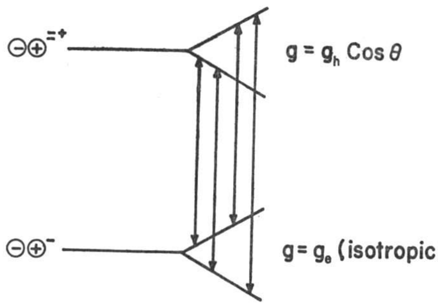

Fig. 3. Donor-Acceptor Complex model. In the lower state, a neutral donor undergoes a molecular-like binding with the charged acceptor to form the donor-acceptor pair. In the upper or excited state, an intrinsic exciton is bound to the pair to form the complex.

the Na and Li-dopants appear to behave as acceptor impurities in the ZnO host lattice. We propose that preferred pairing of the acceptors, with donors which are already present, gives rise to near neighbor pairs. The presence of the acceptor would tend to lower the binding energy of the donor; consequently, the spectral lines would be expected to appear on the high-energy side of the "undoped" line. We further propose that the observed optical transitions arise from excitons bound to donor-acceptor pairs, as shown in Fig. 3. An-inspection of Fig. 3 reveals that the magnetic field splittings of such complexes are very similar to that of neutral donor complexes.[2,3] The polarization of the exciton by the donor-acceptor pair, for certain orientation of the pairs in the lattice, could explain the unexpected orientation dependence observed in Figs. 1(b) and 2(b) for the 3695.40 and 3691.85 Å lines, respectively.

The line multiplicities result from different pair spacings; from different orientations of the donor-acceptor pair; and from excited states of the donor. Williams[4] has pointed out that, for nearest neighbor pairs, the donor electron will be in excited states.

The chemical nature of the donor and acceptor will definitely influence the "probability for preferred pairs", since the mutual electrostatic attraction between different pairs of chemical centers (defects) will be different. This argument could account for the differences in spectral positions (energies) of pair transitions, as well as differences in line intensities, since one member of the pair could be charged. Such arguments could also account for the differences in spectral positions and line intensities, observed for comparable Li and Na doped lines, as shown in Tables I and II. The following argument may be advanced to explain the variation of doped and undoped line intensities with increasing dopant concentration. It is reasonable to assume that, as the concentration of the dopant increases, the pair concentration will also increase but only at the expense of discrete donor sites. Therefore, the intensity of transitions arising from excitons bound to neutral donor sites will decrease as the intensity of transitions arising from excitons bound to paired sites increases.

References

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2) D. C. Reynolds, C. W. Litton and T. C. Collins: Phys. Rev. **140** (1965) A1726.
3) D. G. Thomas and J. J. Hopfield: Phys. Rev. **128** (1962) 2135.
4) F. E. Williams: J. Opt. Soc. Amer. **47** (1957) 869; F. E. Williams: J. Phys. Chem. Solids **12** (1960) 265.

DISCUSSION

Landsberg, P. T.: Have you performed any experiments on the decay kinetics to confirm the pair model ? More generally, I should also like to know whether the recent doubt as to whether ZnO is a direct gap semiconductor has now been cleared up.

Park, Y. S.: I. We have not measured the decay time of these lines. II. On the basis of exciton spectrum of ZnO analysed by us and Thomas, ZnO crystals are direct gap materials.

Otsuka, E.: The condition of charge neutrality requires presence of holes somewhere. Are they free in the valence band or trapped somewhere ?

Park, Y. S.: There are other complexes which were not studied here which account for this.