Review
Associated point defects in II-VI compounds

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Recently, the structures of many associates of point defects in the II-VI compounds have been determined. The status of present knowledge is reviewed with emphasis on the arguments leading to models for the various associates.

1. Introduction
In the last several years the microscopic structures of many defects in crystalline solids have been elucidated by optical, magnetic resonance, electrical, and chemical experiments. The defect state of solids has proved to be quite complex. As well as isolated native defects and isolated dopant atoms, associates of these defects often occur forming what can usefully be considered small molecules embedded in the crystal. The formation of associates can drastically affect the electrical and optical properties of crystals. Improved understanding of association phenomena should lead to greater ease in tailoring materials for desired properties.

This paper reviews the experimental results obtained for associated point defects in the II-VI compounds, the chalcogenides of zinc and cadmium. The mercury compounds are excluded. CdO will also be excluded because of its different crystal structure. The compounds of interest normally have either the sphalerite or wurtzite crystal structure. Both are four-co-ordinated structures. In the cubic sphalerite structure shown in Fig. 1 the neighbours of a cation site are a first shell of four anions along 〈111〉 directions, a second shell of twelve cations along 〈110〉 axes, a third shell of twelve anions along 〈311〉 directions, etc. The wurtzite structure is somewhat similar but has hexagonal symmetry. A large number of associate types has been discovered in these compounds, perhaps largely because they have certain properties which have made the experiments more fruitful.

An associate will be defined as a close grouping of two or more simple defects, where a simple defect is taken to be an atom of the host crystal not on its normal site, a vacancy, or a foreign atom. Thus donor-acceptor pairs separated by many lattice spacings [1] are not considered. Electrons or holes trapped by cations or anions of the host lattice will not be considered simple defects; this restriction excludes, for example, the centre in ZnO consisting of a substitutional lithium and a hole trapped on a nearest-neighbour oxygen [2].

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In the next section, a brief outline of the chemical theory of association of defects is given. The third section discusses the most useful experimental techniques. The fourth part reviews the experimental results and also contains a few new, previously unpublished, observations. Some of the associates will seem to have rather surprising, unexpected structures. In order that the review be of interest to the general reader, much of the detailed data will not be included, but only enough to show how the structures of the associates are deduced.

2. Chemical theory of association
Suppose two simple defects A and B form an associate AB with an enthalpy change $\Delta H$ according to the reaction

$$A + B \rightleftharpoons AB + \Delta H.$$  

If the simple defects and the associates are assumed to be randomly distributed, the concentrations are related by the mass action law

$$[AB][A]^{-1}[B]^{-1} = \exp(-\Delta G/kT),$$  

where $\Delta G = \Delta H - T\Delta S$ is the corresponding change in Gibbs free energy. The entropy change, $\Delta S$, depends largely upon the number of equivalent arrangements possible for the associate, and the enthalpy change $\Delta H$ is due to the interaction between A and B-electrostatic, covalent bonding, short range repulsion, etc [3]. For the case of oppositely charged defects interacting only by Coulomb attraction the distribution of B defects about an A defect as a function of distance from A has been found by several workers. In one derivation, use is made of the mass action law and the crystal is treated as a continuum [4], while another is based on more fundamental probabilistic considerations, and the discrete nature of the crystal lattice is taken into account [5]. The results of both treatments are very similar, however. The distribution has two peaks, one near the distance of closest approach and another near the separation expected for a completely random distribution. These peaks are separated by a minimum at the distance where the interaction energy is equal to the thermal energy $2kT$. If the binding energy is greater than $2kT$, then, there is a tendency toward association. The actual situation in a polar solid is more complex, involving polarization, rearrangement of nearby atoms, and covalent effects, but the simple model gives a good qualitative description of association.

If A and B are two oppositely charged impurity ions of equal total concentration interacting only by Coulomb attraction, Equation 1 can be used to calculate the fraction paired at each of the possible separations (nearest neighbour, third nearest neighbour, etc)

$$\Delta H = -q^2/\varepsilon r,$$  

where $q$ and $-q$ are the charges of the two ions with separation $r$. The interaction is screened by the dielectric constant $\varepsilon$ of the material. Often only the two or three smallest separations need be considered, since almost the whole contribution to pairing comes from these [6]. For example, the fraction paired at separation $r_j$ will be much larger than the fraction paired at the larger separation $r_k$ if

$$(q^2/\varepsilon kT)(r_j^{-1} - r_k^{-1}) \gg 1.$$  

The fraction paired depends strongly on the total concentration $[A] + [AB]$ and on the temperature. At low concentration a large fraction can be paired only at low temperatures. As concentration increases, appreciable pairing can occur at higher temperatures. Of course, pairing at low temperatures may occur so slowly, because the defects may have very low mobility, that it would not be observable. Interstitial atoms can be mobile at very low temperatures [7], however, and associates involving interstitials should form more readily. The time development of the approach to an equilibrium situation in pairing has been treated by Reiss et al [4]. Electrically neutral defects may also form associates; they may exchange an electron to become charged and then interact electrostatically [3].

Even a crystal free from impurity atoms will always contain a number of native defects at non-zero temperature, since the creation of a vacancy, for example, requires only a finite amount of energy. A substitutional impurity is incorporated by interaction with a vacancy. The vacancy concentration affects the solubility of the impurity. Diffusion of impurities usually also requires the presence of vacancies.

Donor or acceptor impurities introduced into II-VI compounds are always largely compensated by native defects. This self-compensation has been explained in the following way [8]. Energy must be supplied by the crystal to produce the compensating native defects, while energy is gained by the interaction of the native defects with the free carriers produced by the