Pairing of Electrons by a Point Defect in c-As_2Se_3

Eugen Tarnow, M. C. Payne,[a] and J. D. Joannopoulos

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 14 July 1988)

By use of *ab initio* density-functional total-energy calculations a point defect with a negative Hubbard U is identified, for the first time, in a chalcogenide system. It is found that in c-As_2Se_3 two noninteracting neutral Se antisite defects are unstable toward the formation of a pair of noninteracting oppositely charged Se antisites. The correlation energy gained is 0.3 eV per electron pair.

PACS numbers: 71.55.Gs, 61.70.At, 71.25.Tn, 71.38.+i

The chalcogenide crystals are semiconducting solids that differ from the simpler tetrahedrally bonded group IV, III-V, or II-VI compounds in two important aspects. First, the molecular nature of the crystals, in combination with the low average coordination number, gives rise to very flexible structures. Second, the top of the valence band consists of nonbonding orbitals that are prone to forming bonds with any available atoms. The flexibility of the structure and the reactiveness of the nonbonding electrons lowers the formation energy of point defects in the chalcogenides and introduces a strong coupling between the electronic states of the defects and their geometric structure. In this paper, we perform *ab initio* total-energy calculations using a molecular-dynamics approach to identify a low-energy point defect with an electron-phonon-coupling-induced *negative* effective correlation energy (negative U).[1-5]

Although the existence of negative-U defects has been *directly* confirmed by experiment,[4] their microscopic structure has so far remained elusive. The defects were first suggested to be dangling bonds that in a positively charged state (D^+) would react with neighboring nonbonding orbitals to make a bond. In a negatively charged state (D^-), the dangling bond would be filled and remain nonbonding, and in the neutral configuration (D^0) they would exist in some "mixed" bonding-nonbonding state. The negative U would result from the reaction

$$2D^0 \rightarrow D^+ + D^-, \tag{1}$$

which was assumed to be exothermic.[2] This type of defect reaction was then studied in a simple chemical bonding picture, and it was suggested that an overcoordinated chalcogen atom defect $C_2{}^0C_3{}^0$ (where $C_n{}^q$ stands for an n-fold coordinated chalcogenide atom with charge q) should have a negative U[3]; i.e., two of these defects would lower their combined energy through the reaction

$$2C_2{}^2C_3{}^0 \rightarrow C_2{}^0C_3{}^+ + C_1{}^-C_2{}^0. \tag{2}$$

After these suggestions, realistic *ab initio* calculations were carried out to investigate the nature of the $C_2{}^0C_3{}^0$ defects.[5] Since these calculations are computationally very demanding, one is forced to focus on the simplest homopolar chalcogenide Se. The results of the calculation were surprising. It was found that in both crystalline and glassy Se the $C_2{}^0C_3{}^0$ defects should have a *positive* U.[5] It was argued, however, that for the compound chalcogenides, the larger dielectric constant and anticipated greater extent of the $C_1{}^-C_2{}^0$ defect state, might still lead to an overall negative U.[5]

Even though more than ten years have passed since the introduction of the idea for negative U defects in chalcogenides, realistic theoretical calculations have been intractable because of the complexity of the heteropolar materials. In particular, the suggested negative U of the $C_2{}^0C_3{}^0$ defects has therefore remained unconfirmed. With the present contributions we establish, using the same type of theory that predicted positive U defects in Se,[5] the microscopic structure of a *negative-U* point defect in a prototype heteropolar chalcogenide material, As_2Se_3. To make the calculations feasible, we investigate the crystalline material where the geometry considerably restricts the possible types of defects. For example, although in the glass the $C_3{}^0$ defect may have zero, one, two, or three nearest Se neighbors, in the crystal the $C_3{}^0$ defect is an antisite that always has three Se nearest neighbors. The latter defect, a Se antisite in c-As_2Se_3, which is a member of the $C_2{}^0C_3{}^0$ class of defects, is the defect we report in this paper.

Briefly, the technical details of our investigation are as follows. The calculations are based on the *ab initio* density-functional pseudopotential method in which we used local pseudopotentials of the Starkloff-Joannopoulos form.[6] We took advantage of the modified Car-Parrinello scheme[7,8] for the electronic relaxation and allowed full movement of all atomic coordinates. To model an isolated defect the supercell approximation was used with one antisite defect every forty atoms. The special k point $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ was used for performing the averages over the Brillouin zone. As a consequence of these approximations we estimate that the total energies should be accurate to within 20% and the computed effective correlation energy to within 30%.[9]

We begin our analysis by examining the crystal struc-

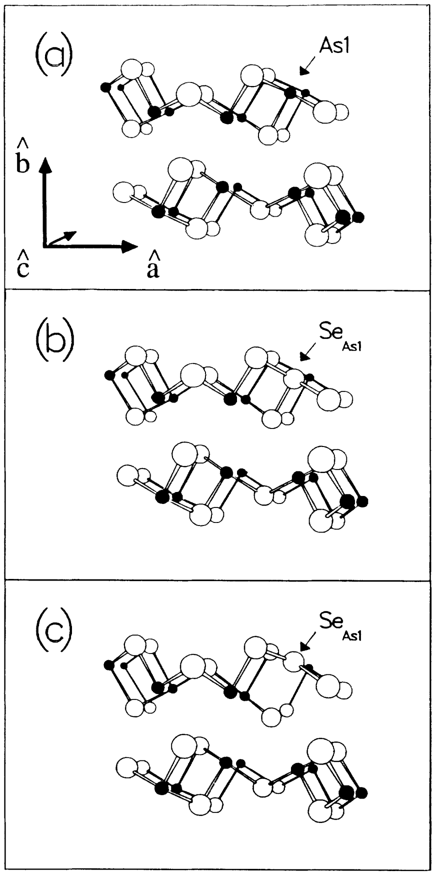

FIG. 1. (a) Three-dimensional schematic illustration of the structure of c-As_2Se_3. The material forms in layers that lie perpendicular to the plane of the figure. Within a layer As and Se atoms (black and white in the figure) of types 1 and 2 form spiraling chains running perpendicular to the figure. Neighboring chains are linked together by Se atoms of type 3. The lattice vectors of the crystal are indicated in the lower left-hand corner. The figure shows the forty-atom supercell used for the defect calculation. The supercell volume is that of two crystal unit cells. The atom that will form the antisite is indicated. (b) Structure of the relaxed, positively charged Se antisite defect (Se_3^+). (c) Structure of the relaxed negatively charged Se antisite defect (Se_1^-). Notice that a bond has been broken (elongated to 2.96 Å).

ture of c-As_2Se_3.[10] This is shown in Fig. 1(a). We note that the material forms layers running perpendicular to the plane of the figure. Each layer consists of helical chains of alternating As and Se atoms and these chains are bonded together by bridging Se atoms. The unit cell is nearly orthorhombic and is defined by the lattice vectors **a**,**b**,**c**. There are twenty atoms in the unit cell, but only two As atoms and three Se atoms are chemically inequivalent. Figure 1(a) shows forty atoms, or two unit cells, corresponding to the supercell we used in the defect calculations.

The calculation proceeds as follows. The theoretical structure of the crystalline state is obtained by our start-

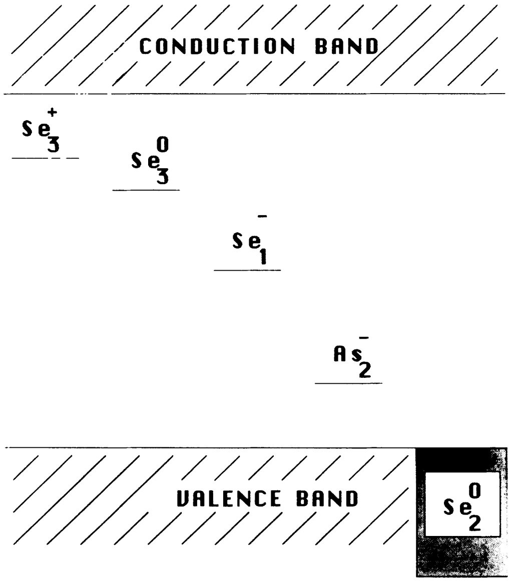

FIG. 2. Calculated electronic levels associated with the three charge states of the Se antisite defect (Se_3^+, Se_3^0, and Se_1^-), the As antisite defect (As_2^-) and, for reference, the Se nonbonding band appearing in the perfect crystal (Se_2^0).

ing from the experimentally determined structure as an initial guess. Small movements away from the experimental structure take place before the theoretical equilibrium configuration is established. The agreement with experiment[10] is excellent—the worst deviation being 5% in the lattice constant in the a direction.

The next step of the calculation is to substitute a Se atom for the As1 atom as indicated in Fig. 1(b) and let the new structure relax. By allowing the electronic occupation to vary we model different charge states of the defect. Let us consider each of three charge states separately.

The positively charged defect relaxes without any large movements from its "perfect" antisite position [Fig. 1(a)]. It introduces a level in the gap right below the conduction band (Fig. 2, level Se_3^+). This is consistent with a Se—Se antibonding state. In a chemical bonding picture, the state should be localized on the four central Se atoms, but because of the large screening in the material (the static dielectric constant[11] is about 10) it becomes more spread out. An examination of the charge densities reveals that only 42% of the state is found around the four Se atoms.

The neutral defect relaxes to a configuration in which one of the bond lengths has increased from 2.35 to 2.55 Å. The singly occupied electronic state in the gap moves down somewhat from the state of the charged configuration (Fig. 2, level Se_3^0). This level is consistent with an electron trap level found in experiment at 0.6 eV below the conduction band.[12]

Finally, the negatively charged defect relaxes by further stretching the elongated bond and increasing the distance between the two atoms to 2.96 Å [Fig. 1(c)]. The electronic state in the gap moves to about midgap (Fig. 2, level $\mathrm{Se}_1{}^-$), consistent with an electron trap level found by experiment at 1.0 eV below the conduction band.[12] This level is somewhat concentrated around a filled nonbonding orbital of the onefold coordinated Se atom (25% of the state) and on the (now) twofold coordinated antisite (20% of the state).

In a chemical-bonding picture we would identify the three defect states as follows. Initially, the positively charged defect is a threefold-coordinated Se atom with all its bonding states filled and all its antibonding states empty. When we add one electron, this electron goes into the antibonding state. No bonds are broken, however, since having two electrons in a bonding state and one in an antibonding state is more energetically favorable than having all three electrons in nonbonding states. When we finally add the last electron, there are two electrons in the antibonding state and, according to earlier predictions,[3,13] one of the bonds breaks and the defect forms one twofold- and one onefold-coordinated Se atom. The chemical bond picture is, however, only a first approximation for the following reasons: (i) the elongated bond of the negatively charged state has a charge density associated with it that is not very different from the positively charged state, suggesting that the bond does not break completely; (ii) the nonbonding level of the onefold-coordinated Se atom is found at about midgap rather than, as suggested by the chemical bond picture, at the top of the valence band; (iii) only 25% of this midgap level is localized on the onefold-coordinated Se atom rather than 100%; (iv) and, finally, we find that the screening in this material is so large that, for example, the onefold-coordinated Se atom is neutral (within a sphere of radius 1.5 Å) to about $\frac{1}{10}$ of an electron rather than having the charge of -1.

We are now ready to accomplish the main objective of this paper: to compute the effective electronic correlation energy for the antisite defect. It is defined as the energy released in the reaction (2):

$$U_{\mathrm{eff}}(\text{Se antisite}) = 2E_{\mathrm{TOT}}(C_2{}^0C_3{}^0) - E_{\mathrm{TOT}}(C_2{}^0C_3{}^+) - E_{\mathrm{TOT}}(C_1{}^-C_2{}^0). \tag{3}$$

We find that $U_{\mathrm{eff}}(\text{Se antisite}) = -0.28 \pm 0.08$ eV. This consists of a Coulomb term ~0.2 eV and a defect relaxation term ~ −0.5 eV. To investigate the dependence of the correlation energy on the defect environment we recalculated the U for a configuration in which the layers of the material are separated from each other by about 6 Å. This should reduce the effects of defect-defect interactions as well as model a variation in density that might be relevant to the glass. We find a U of -0.31 eV, very similar to our previous result. Thus we have demonstrated that the Se antisite is a negative U defect.

We did find an interesting change in the U when we allowed two antisite defects to interact with one another to form an intimate valence alternation pair.[3] This made the U less negative by about 0.14 eV for the first added electron pair, while the U remained the same (0.3 eV) for the second electron pair. Thus we conclude that in the crystal there is a negative effective electronic *pair-pair* correlation energy associated with any existing intimate valence alternation pair.

In order to detect the negative U defects experimentally, for example, by a pinning of the Fermi level, it is necessary that the defects exist in large numbers. Let us examine if this is the case. The concentration of the defects depends upon the free energy of the defects and the crystal growth temperature. The free energy of the Se antisite is sensitive to the particular atomic reservoirs chosen. If we take the atomic reservoir to be c-$\mathrm{As_2Se_3}$, in order to make a Se antisite we must also make an As antisite, and the formation energy we calculate is the formation energy of the pair of opposite antisites. The formation energy we obtain is 1.9 ± 0.4 eV.[14] Including the entropy of mixing we can determine the concentration of separate antisites by a Bolzmann factor in which the energy is $\frac{1}{2}$ of 1.9 eV. At the growth temperature 650 K,[15] this results in $10^{15\pm1}$ defects/cm^3. However, it is important to note that it is difficult to prepare a crystal under precise stoichiometric conditions, so that either type of antisite may be more probable than the other.

Are there any other negative U defects in the crystal? The restrictive geometry of the crystal suggests that the Se antisites may be the only prevalent negative U defects for three reasons. First, other low-energy defects probably have a positive U: We found, after a similar calculation to the one above that the As antisite has a positive U of 0.4 eV. Second, other simple defects such as vacancies and interstitials have high formation energies since they involve breaking bonds. (There is one particular vacancy in the crystal that one might expect to self-heal and keep the number of bonds the same; the Se3 vacancy. A calculation was performed on this structure and it was found that the correlation energy was very close to 0.0 eV.) Third, although one can envision defect complexes with a negative U, they have the problem of loss of entropy of mixing which makes them unlikely to appear.

If the Se and As antisites are the prevalent defects in the crystal, the following picture emerges for the pinning of the Fermi level: Depending on the relative numbers of the two defects we have to distinguish two cases. If there are more Se antisites than As antisites, the Fermi energy should be pinned in the middle of the two gap levels resulting from the threefold-coordinated positively charged Se antisite and the onefold-coordinated negatively charged Se antisite. Since the onefold-coordinated nonbonding orbital falls about midgap, the Fermi level should be pinned above midgap, in agreement with experiment.[15] Furthermore, there should be no paramagnetic centers associated with the pinning of the Fermi level.[16] On the other hand, if one had a material in which there are more As antisites than Se antisites, the Fermi level would be pinned below midgap at the As nonbonding level (Fig. 2, level $\mathrm{As}_2{}^-$). Since the As antisites are positive U defects in the crystalline material, a paramagnetic signal would now appear.

We thank Dr. L. Robbins for useful discussions and A. Rappe for a critical reading of the manuscript. This work was supported in part by a National Science Foundation Grant No. DMR84-18718 and the Office of Naval Research Contract No. N000 14-86-K-0158.

---

[a] Now at the TCM group, Cavendish Laboratory, Madingley Road, Cambridge, CB30HE, England.

[1] P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

[2] N. F. Mott, E. A. Davis, and R. A. Street, Philos. Mag. **32**, 961 (1975).

[3] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **35**, 1293 (1975); Marc Kastner and H. Fritzsche, Philos. Mag. B **37**, 199 (1978).

[4] T. Thio, D. Monroe, and M. A. Kastner, Phys. Rev. Lett. **52**, 667 (1983).

[5] David Vanderbilt and J. D. Joannopoulos, Phys. Rev. B **27**, 6311 (1983).

[6] Th. Starkloff and J. D. Joannopoulos, J. Chem. Phys. **68**, 5794 (1978). The parameters used for Se were $\lambda = 10.196$ a.u.$^{-1}$ and $r_c = 0.923$ and for As they were $\lambda = 10.196$ a.u.$^{-1}$ and $r_c = 0.973$. The kinetic energy cutoff for the basis set was 19 Ry corresponding to 10000 plane waves.

[7] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[8] M. C. Payne, J. D. Joannopoulos, D. C. Allan, M. P. Teter, and D. H. Vanderbilt, Phys. Rev. Lett. **56**, 2656 (1986).

[9] The main errors in the total energies come from the k-point averaging of the Brillouin zone (the total energy changed by 18% on increasing the number of k points from 1 to 14) and from the supercell approximation (the Coulomb interaction between supercells contributed 8% to the total energy). Three other approximations—the finite number of plane-wave basis states, the size of the Fourier transform grid, the use of local pseudopotentials—contribute errors of less than 0.1 eV.

[10] A. S. Kanisheva, Yu. N. Mikhailov, E. G. Zhukov, and T. G. Grevtseva, Izv. Akad. Nauk SSSR, Neorg. Mater. **19**, 1981 (1983).

[11] R. Zallen, M. L. Slade, and A. T. Ward, Phys. Rev. B **3**, 4257 (1971).

[12] G. Brunst and G. Weiser, Philos. Mag. B **52**, 843 (1985).

[13] David Vanderbilt and J. D. Joannopoulos, Phys. Rev. B **23**, 2596 (1981).

[14] The corresponding charge configuration has the As antisite negatively charged, and the Se antisite positively charged.

[15] G. Brunst and G. Weiser, Philos. Mag. B **51**, 67 (1985); H. L. Althaus, G. Weiser, and S. Nagel, Phys. Status Solidi (b) **87**, 117 (1978).

[16] The ESR response is less than $10^{16}/\mathrm{cm}^3$ in P. C. Taylor, U. Strom, and S. G. Bishop, Sol. Energy Mater. **8**, 23 (1982).

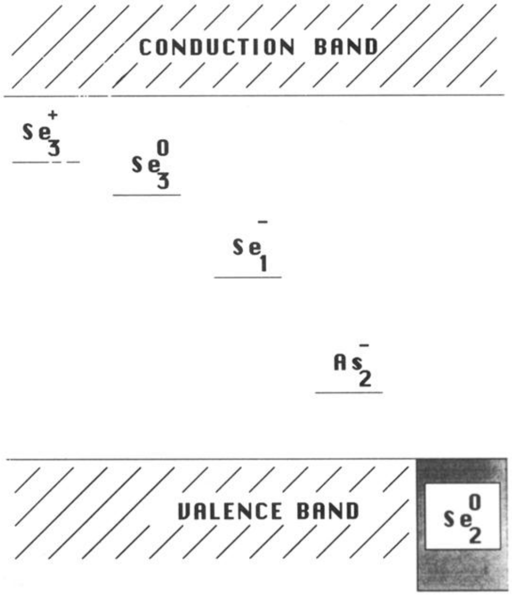

FIG. 2. Calculated electronic levels associated with the three charge states of the Se antisite defect ($Se_3{}^+$, $Se_3{}^0$, and $Se_1{}^-$), the As antisite defect ($As_2{}^-$) and, for reference, the Se nonbonding band appearing in the perfect crystal ($Se_2{}^0$).