

## Bonding Coordination Defect in *g*-Se: A "Positive-*U*" System

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The effective Hubbard  $U$  for the bonding coordination defect in glassy Se is investigated. This is accomplished by applying local-density total-energy calculations directly to charged defects. The existence of a sizable negative contribution to  $U$  from structural relaxation is confirmed. However, a still larger Coulomb repulsion gives rise to an overall *positive*  $U$ . This result is *not* inconsistent with a negative  $U$  in the compound chalcogenide glasses.

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Several years ago, Anderson<sup>1</sup> made a novel proposal to explain the peculiar behavior of chalcogenide glasses. For these materials, experiments have been interpreted to imply a large density of states ( $\sim 10^{17} \text{ cm}^{-3} \text{ eV}^{-1}$ ) pinning the Fermi level near midgap,<sup>2,3</sup> while the number of free spins is much smaller ( $\lesssim 10^{15} \text{ cm}^{-3}$ ).<sup>2-5</sup> Anderson suggested that a strong electron-phonon coupling could give rise to a negative effective Hubbard correlation energy ("negative  $U$ ") which would tend to pair free spins in the material. Mott, Davis, and Street,<sup>6</sup> and Kastner, Adler, and Fritzsche<sup>7</sup> incorporated Anderson's idea into a defect model, in which intrinsic bonding coordination defects are responsible for the negative  $U$ . Other authors proposed competing models based upon a broad distribution of bond strengths<sup>8,9</sup> or upon polarons<sup>10</sup> to explain the experiments. Unfortunately, compelling theoretical arguments for the existence of the negative  $U$  for the defects in the defect model were absent; simple models<sup>7</sup> could not predict the sign of  $U$  for defects in a chalcogenide material. The lack of long-range order and symmetry, the necessity of fully relaxing the defect structures, and the difficulty of dealing with charged defects all presented serious obstacles to the formulation of a realistic theory.

We have recently developed an approach which makes tractable an *ab initio* calculation of the effective  $U$  for the case of glassy Se, the simplest of these materials. Unlike previous approaches,<sup>11</sup> our work is based directly upon the calculation of total energies of neutral and charged defects. We find the Hubbard  $U$  to be *positive* for a bond-

ing coordination defect in this system. After discussing these results, we will argue that the experiments may in fact be consistent with a positive  $U$  for this special case. Our results in no way rule out a negative  $U$  in the more typical compound chalcogenide glasses ( $\text{As}_2\text{Se}_3$ ,  $\text{As}_2\text{S}_3$ , etc.) where the experimental evidence for a negative  $U$  is much stronger.

In the defect model,<sup>6,7</sup> *g*-Se is to a first approximation considered to be a continuous random network consisting of chains (and possibly rings) of two-fold coordinated atoms. The bonding coordination defect consists of a dangling chain end which may take on the charge state  $D^+$ ,  $D^0$ , or  $D^-$ , depending on whether 0, 1, or 2 electrons occupy the gap state. If it is thus the  $D^0$  which is magnetically active. For the  $D^+$ , the chain end is expected to bond to a neighboring chain to form a threefold coordinated ( $C_3^+$ ) defect, while the  $D^-$  is expected to remain singly coordinated ( $C_1^-$ ). Recently, we showed<sup>12</sup> that the neutral defect is also expected to remain singly coordinated ( $C_1^0$ ). The effective Hubbard  $U$  may be defined in terms of total energies as

$$U = E_{\text{tot}}[C_3^+] + E_{\text{tot}}[C_1^-] - 2E_{\text{tot}}[C_1^0]. \quad (1)$$

Thus, if  $2C_1^0 \rightarrow C_3^+ + C_1^-$  is exothermic, there is a negative  $U$ , and the free spins associated with the  $C_1^0$  are purged. Our goal is to calculate  $U$  from Eq. (1).

The approach consists of constructing artificial superlattice structures containing defects, so that the defect and its local environment mimic that of the glass. The total energies and Hellman-Feynman forces<sup>13</sup> are then calculated in the fro-

zen-core and local-density approximations.<sup>14</sup> The extension to the much more complex case of charged defects is made here for the first time. The forces are used to relax the structure to its lowest energy configuration for each of the three relevant charge states. (The details of the method will be described elsewhere.<sup>15</sup>) Finally, total energies are used to evaluate Eq. (1).

Because of topological constraints and the necessity of keeping a net neutral charge in the unit cell, we are required to deal with *pairs* of defects in each unit cell. Note that Eq. (1) can be rewritten in terms of defect pairs as

$$U = E_{\text{tot}}[C_3^+C_1^-] - E_{\text{tot}}[C_1^0C_1^0]. \quad (2)$$

This is valid as long as the two defects which make up a pair are noninteracting (distant). For the superlattice structures, corrections for the effects of interdefect interactions must be introduced.

Two different supercell geometries are considered to ensure that the details of the interchain coupling do not crucially affect the results. Geometry I is made by removing an atom to form a vacancy at every ninth site along a chain in trigonal Se, as shown in Fig. 1. It thus allows us to study the interconversion between  $C_1^0C_1^0$ , Fig. 1(a), and  $C_3^+C_1^-$ , Fig. 1(b). Geometry II, not shown, differs only in detail: It has a larger unit cell made by creating a vacancy at every twelfth site. Both geometries allow Eq. (2) to be eval-

uated directly.

There are three kinds of interdefect interactions which must be eliminated to model distant defects. Firstly, there is the Coulomb interaction between the charge clouds of different charged defects. Since these are arranged on a superlattice of alternating positive and negative sites, this correction is given to lowest order by the Madelung energy of point charges on the same lattice, embedded in a uniform dielectric. Corrections for the  $q$  dependence of  $\epsilon$  and the extent of the charge clouds are then introduced.<sup>15</sup> Secondly, the hopping matrix elements between different defect state wave functions cause hybridization into bonding and antibonding combinations of defect states. The Fermi level falls so that only the bonding combinations are occupied, lowering the total energy. This can be effectively corrected by specifying the appropriate occupation numbers in generating the screening potential using a density matrix formalism.<sup>16</sup> Thirdly, the effects of spin polarization for  $C_1^0$  defects must be taken into account by using a spin-dependent local density functional.<sup>17</sup>

We have also tested how the structural relaxation energy changes when the constraints arising from periodic boundary conditions are removed. This can be modeled effectively by monitoring the trend in relaxation energy as one goes to larger unit cells. By using a simple, yet very accurate, force-constant Hamiltonian<sup>18</sup> and cells up to 72 atoms, it was found that the change in relaxation energy is only about 0.05 eV from geometry I and is thus unimportant.

We proceed now to the results, which will be presented in more detail elsewhere.<sup>15</sup> We confirm that the lowest-energy  $D^+$ ,  $D^0$ , and  $D^-$  defects are  $C_3^+$ ,  $C_1^0$ , and  $C_1^-$ , as expected. The resulting values for the effective Hubbard  $U$  are shown in Table I. The "uncorrected" value is the energy per cell to transfer a charge simultaneously in each unit cell of the superlattice structure. This energy contains the spurious interdefect Coulomb interactions, and is lower for geometry I because each negative defect is well screened by surrounding positive defects and vice versa. For geometry II, on the other hand, the oppositely charged defects are roughly segregated into layers, so that repulsive interactions are more prevalent. This is reflected in a much smaller Madelung correction for geometry II (second entry of Table I). This is an advantage for geometry II because of the large uncertainty in the Madelung correction; this geometry

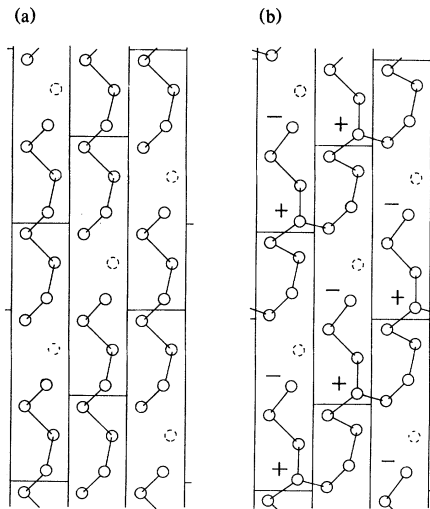


FIG. 1. Supercell geometry I, made by creating a vacancy (open circles) at every ninth site in the trigonal Se structure. (a) Relaxed structure before charge transfer, containing two  $C_1^0$  defects. (b) Relaxed structure after charge transfer, containing  $C_3^+$  and  $C_1^-$ .

TABLE I. Contributions to the effective Hubbard  $U$ . Three corrections  $\Delta U$  correspond to effects of subtracting out interdefect interactions (see text). Error estimates indicate theoretical uncertainty due to sources other than the frozen-core and local-density approximations.

|                              | Geometry I<br>(eV) | Geometry II<br>(eV) |
|------------------------------|--------------------|---------------------|
| Uncorrected $U$              | $0.10 \pm 0.12$    | $0.42 \pm 0.12$     |
| Madelung $\Delta U$          | $0.71 \pm 0.25$    | $0.16 \pm 0.04$     |
| Density matrix $\Delta U$    | $-0.34 \pm 0.03$   | $-0.39 \pm 0.03$    |
| Spin polarization $\Delta U$ | $0.19 \pm 0.02$    | $0.16 \pm 0.02$     |
| Total corrected $U$          | $0.66 \pm 0.28$    | $0.35 \pm 0.13$     |

was in fact chosen for this reason. In order to make a physically meaningful comparison between the energies of geometries I and II, one must include this correction; the subtotals for geometries I and II are then in closer agreement,  $\sim 0.8$  and  $\sim 0.6$  eV, respectively, with more confidence assigned to the latter value. The density-matrix and spin-polarization corrections are seen to be roughly the same for the two geometries. Even allowing the most unfavorable error estimates, Table I clearly show a positive overall  $U$  in both cases.

While a  $U$  of  $\sim 0.45$  eV falls comfortably within both error ranges, it is quite possible that the difference between the  $U$  for geometries I and II is real. Some variation in  $U$  for defects in the glass should be expected, since the details of the local structural environment will be different for each defect, just as it is different for geometries I and II. If the distribution of  $U$  values is wide, a few may be negative, but the absence of free spins cannot be explained unless almost all are negative.

To see physically how a positive  $U$  comes about, consider the configuration coordinate diagram for a pair of distant defects, shown in Fig. 2. The neutral defects relax to the structure  $C_1^0 C_1^0$ . A calculation of the total energy for the same geometry after charge transfer shows that it then costs  $\sim 1.1$  eV to transfer an electron from one defect to the other. Most of this energy ( $\sim 0.9$  eV) is attributable to the Coulomb repulsion of putting a second electron on the dangling bond of the  $C_1^-$ . The system then relaxes to the  $C_3^+ C_1^-$  configuration, lowering its energy by  $\sim 0.5$  eV in the process. Thus, we see that the qualitative features of the defect model are confirmed: The positively charged dangling bond *does* relax to

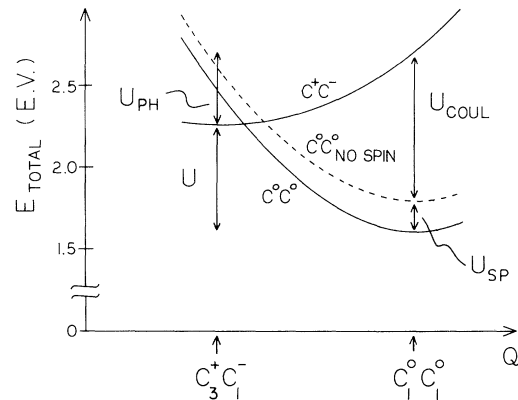


FIG. 2. Configuration coordinate diagram for a distant pair of defects, as derived from geometry I. Solid lines show total energy for neutral and charged cases; dashed line shows neutral case without spin polarization. The total effective  $U$  is a sum of positive Coulomb ( $U_{\text{Coul}}$ ) and spin-polarization ( $U_{\text{sp}}$ ) contributions and a negative phonon ( $U_{\text{ph}}$ ) or structural relaxation contribution.

form an extraordinary bond, and this *does* give rise to a large negative contribution ( $\sim -0.5$  eV) to the effective  $U$ . However, the Coulomb interaction gives rise to a larger positive contribution.

Among the chalcogenide glasses, experiments indicate<sup>19-21</sup> that Se has an unusually low density of deep midgap states,  $\leq 2 \times 10^{14}$  cm<sup>-3</sup>. This value is compatible with the upper bounds on free spins,<sup>2-5</sup> and thus with a positive  $U$ . If  $U$  is positive for  $g$ -Se but negative for the compound chalcogenides, this could be understood as follows. First,  $g$ -Se has a relatively low static dielectric constant of  $\epsilon = 6.6$  compared, e.g., with 12-20 for the series  $\text{As}_2\text{Se}_x\text{Te}_{3-x}$ .<sup>22</sup> Second, the defect wave function for  $C_1$  in  $g$ -Se is much more localized than in  $g$ - $\text{As}_2\text{Se}_3$ .<sup>23</sup> Since the Coulomb contribution  $U_{\text{Coul}}$  to the effective  $U$  scales as  $U_{\text{Coul}} \propto \epsilon^{-1} L^{-1}$ , where  $L$  is the extent of the defect state,  $U$  is in fact expected to be more positive in Se than in the other chalcogenides.

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## Dimensionality in *bis*-Tetramethylselenafulvalenium Hexafluorophosphate, (TMTSF)<sub>2</sub>PF<sub>6</sub>

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The dimensionality of the spin dynamics in *bis*-tetramethylselenafulvalenium hexafluorophosphate (TMTSF)<sub>2</sub>PF<sub>6</sub>, is studied in the high-pressure metallic phase at low temperatures via the field dependence of proton relaxation rates. Two regimes are identified: a low-field regime (1–12 kOe) where the relaxation rate is independent of field and a high-field regime (12–120 kOe) where the relaxation rate depends logarithmically on field. The high-field behavior is interpreted as spin dynamics in a quasi two-dimensional metal with a crossover to three-dimensional spin dynamics at low field.

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The organic metal *bis*-tetramethylselenafulvalenium hexafluorophosphate, (TMTSF)<sub>2</sub>PF<sub>6</sub>, has recently been under intense experimental scrutiny as a result of the observation of superconductivity under pressure,<sup>1</sup> the existence of a spin-density wave<sup>2</sup> (SDW) at lower pressure, and the possibility of superconducting fluctuations to 40 K,<sup>3</sup> well above *T<sub>c</sub>*. The speculation that one-dimensional (1D) superconducting fluctuations persist at such

high temperature accounts for the paramount importance of establishing the dimensionality of electronic transport in this system. The motivation of this present work is to use a direct probe of the spin dynamics to establish the dimensionality of the Fermi surface. The results show that (TMTSF)<sub>2</sub>PF<sub>6</sub> is a 2D metal in the high-pressure phase.

Nuclear magnetic resonance (NMR) relaxation