

Formation of negative- U centers in ionic crystals

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(Received 26 August 1981)

It is argued that a natural tendency exists for multivalent impurities in an ionic host crystal to act as negative- U centers. The tendency is due to an increase in the impurity-host lattice attractive interaction when the impurity is in the donor state which is greater than the decrease in interaction in the acceptor state. Differences in lattice distortions are responsible for this difference. Results of a model calculation for Group III impurities in PbTe support the above contention.

The existence of "negative- U centers" was first proposed by Anderson¹ in order to explain the absence of paramagnetism in certain amorphous solids. The idea was extended and made more concrete by Street and Mott² and by Mott, Street, and Davis³ in order to explain the insensitivity to doping of certain chalcogenides. A negative- U center is an impurity or imperfection which forms a state in the gap of a semiconductor and prefers to be either empty or doubly occupied. Such behavior is in contrast to that of an ordinary impurity of imperfection (a "positive- U center") which is either empty or singly occupied. (The symbol " U " stands for the correlation energy of the two electrons and will be discussed below.) Consider the following reaction:



I^0 represents the center in its neutral state relative to the lattice; the neutral state does not mean that the impurity is not ionized; it merely carries the same charge as the host atom which it replaces. I^+ represents the donor state since the impurity has given off an electron, and I^- represents the acceptor state since the center has acquired an electron. As in Ref. 3, let W_1 be the energy to take an electron from the center to the conduction band, i.e., the energy for the process $I^0 \rightarrow I^+ + e$. Next, let W_2 be the energy for the process to take an electron from the valence band and localize it on the impurity, i.e., the process $I^0 + e = I^-$. If there is no lattice reaction W_2 must be $E_G - W_1 + U_{\text{Coul}}$, where E_G is the band-gap energy and U_{Coul} is the energy due to the Coulomb repulsion between electrons localized on the same site. The total energy for reaction (1) in the absence of lattice reaction is given by

$$\begin{aligned} U_0 &= W_1 + W_2 - E_G \\ &= W_1 + E_G - W_1 + U_{\text{Coul}} - E_G = U_{\text{Coul}} \end{aligned} \quad (2a)$$

The reason for subtracting E_G from $W_1 + W_2$ is that the band-gap energy is recovered when the electron and hole recombine. Since U_{Coul} is positive, the en-

ergy U_0 is positive and, therefore, reaction (1) will not occur. Suppose, however, that the transfer of an electron from the center to the conduction band results in an additional energy term ΔW_1 and that the transfer of an electron from the valence band to the center results in an additional energy ΔW_2 , as a result of lattice "reaction" or "relaxation." The lattice reaction may take the form of displacement of host atoms from their normal positions as well as the rearrangement of the charge distribution on these atoms. The energy for reaction (1) in the presence of lattice relaxation thus becomes

$$U = \Delta W_1 + \Delta W_2 + U_{\text{Coul}} \quad (2b)$$

Clearly, in order for reaction (1) to occur spontaneously ($\Delta W_1 + \Delta W_2$) has to be negative and numerically greater than U_{Coul} . For a shallow impurity in a covalent semiconductor ΔW_1 and ΔW_2 will be negligible since the electron (hole) is in a very extended orbit. Hence, ionization of the carrier or addition of a second carrier has a negligible effect on the lattice so that $U \approx U_{\text{Coul}}$ and is therefore positive. However, in a few systems, with deep impurities, it has been postulated that U is negative so that autocompensation results with pinning of the Fermi level.²⁻⁸

In this Communication we wish to point out that there is a natural tendency toward negative- U -center behavior in certain ionic crystals doped with multivalent impurities, and that one can make semiquantitative estimates of the lattice distortions which cause this behavior. The tendency toward such behavior results from the following asymmetry: *The gain in energy, ΔW_1 , when the lattice shrinks around the empty donor state is greater than the cost in energy, ΔW_2 , when it expands around the doubly occupied acceptor state.* The simplest case to consider is an ionic lattice $A^{2+}B^{2-}$ doped with an impurity which substitutes for A . The impurity must be able to give off one, two, or three electrons to the lattice. In the simplest picture of an ionic solid the valence band is made up of atomic orbitals of an anion and the conduction band from orbitals of the cation.⁹ Hence, if the impurity

gives off only one electron to the valence band it will act as an acceptor since the host ion which it replaces gives off two electrons. If the impurity gives off two electrons it will be electrically neutral, and if it gives off three electrons two will fill the valence band and the third will go into the conduction band so that donor action will result. The ionic charge on the impurity will be +1, +2, and +3 for acceptor, neutral, and donor action but the charge relative to the lattice will be -1, 0, and +1 for the three cases. We now start with the impurity in the neutral state and ask whether a tendency toward autocompensation exists. As the charge relative to the lattice changes from 0 to ± 1 an electric field is produced which will induce dipoles on the host ions, just as in the case of a covalent host crystal. In an ionic host, however, the electric field will produce additional dipoles due to the displacement of host ions from their normal positions. Donor action, for example, produces a positive charge which pulls anions toward the center and pushes cations away. Since the nearest neighbors are anions the lattice will tend to shrink around the center. By an analogous argument acceptor action will tend to expand the lattice around the center. We now write the potential at the impurity site as $-q/R$ where R is an effective cavity radius chosen so as to give the correct potential. Thus, R_0 would be chosen so as to give the Madelung potential appropriate to the neutral state, R_D and R_A would be suitable chosen radii for the donor and acceptor states, respectively. Clearly, if $R_D = R_0 = R_A$ no change in lattice energy is produced by reaction (1) since the energy change $-q^2/R + q^2/R$ equals zero. (The negative sign arises from the fact that for the donor state the effective charge of the center is +1, while for the acceptor state it is -1.) However, because of the shrinkage of the lattice for the donor case $R_D < R_A$, and hence the lattice energy change will favor reaction (1).

Fortunately, for an ionic lattice these qualitative arguments can be strengthened by fairly realistic estimates of the lattice distortions, subject to only one assumption: Exchange forces between the electron or electrons on the impurity site and host ion electrons can be neglected. In practice this means that the energy of the electron or electrons on the impurity does not overlap with one of the energy bands of the host crystal. It is relatively easy to calculate the lattice distortions with the method developed by Brauer.¹⁰ The method is described in the original paper as well as in a review paper by Lidiard¹¹ and in a recent paper by the author.¹² Basically, Brauer attempts to find the equilibrium position of the host ions which are acted upon by electrical forces and by repulsive forces which originate from closed-shell interactions. The electrical forces originate from the effective charge on the impurity and from those dipoles which are due to displacement of ions and

those which are due to the redistribution of electrons on the ions. The repulsive forces counteract the electrical forces which tend to push cations and anions toward each other. After finding the displacements in a self-consistent way the change in electrostatic energy and strain energy caused by a change in charge state of the impurity is readily obtained. The energy for the lattice reaction ΔW_1 and ΔW_2 of Eq. (2a) thus become

$$\Delta W_1 = -3(\phi_D - \phi_D^0) + \Delta W_D^{\text{St}} = \Delta\phi_D + W_D^{\text{St}} \quad (3a)$$

$$\Delta W_2 = -\phi_A + \phi_A^0 + W_A^{\text{St}} = \Delta\phi_A + W_A^{\text{St}} \quad (3b)$$

so that the energy for reaction (1) becomes

$$U = \Delta\phi_D + \Delta\phi_A + W_D^{\text{St}} + W_A^{\text{St}} + U_{\text{Coul}} \quad (3c)$$

Here ϕ_D and ϕ_A are the electrostatic potentials at the impurity site in its donor state D (charge 3+) and acceptor state (charge 1+), respectively. The ϕ^0 's are analogous potentials calculated without allowing ions to move and assuming the same radius for the impurity and the host ion it replaces. ΔW^{St} is the strain energy due to differences in radii and due to motion of ions.

To illustrate the use of Brauer's method for the purpose of investigating whether certain multivalent impurities can behave as negative- U centers in an ionic host we cite some results of recent calculations by the author on the behavior of Group III elements in lead telluride.¹² (The aim of these calculations was to understand n - and p -type behavior of these elements, but upon further reflection it became clear that the results can also shed light on the tendency toward negative- U -center behavior.) We refer the reader to Ref. 12 for details as to the choice of parameters as well as for the justification of treating PbTe as an ionic crystal. In Table I we list the results for In for two values of the repulsion parameter ρ . The values for the columns of Table I are based on Table II ($\rho = 0.38 \text{ \AA}$) and on Table III ($\rho = 0.34 \text{ \AA}$, or 0.36 \AA), respectively, of Ref. 12. To obtain $q\Delta\phi_D$ ($= -3\phi_D + 2\phi_0$) we subtracted twice the Madelung energy $q\phi_0$ of a divalent NaCl lattice from columns (a) of the entries marked "ionic energy donors" in Tables II and III of Ref. 12. To obtain $q\Delta\phi_A$ ($= \phi_A + 2\phi_0$) we subtracted twice the Madelung energy from columns (a) of the entries marked "ionic energy acceptors." The strain energies W_D^{St} and W_A^{St} are taken from columns (b) of the entries marked ionic energy donors and ionic energy acceptors, respectively. The column U_{latt} in Table I is the algebraic sum of columns (1) to (4). U_{Coul} is the repulsive energy between two electrons on the In s level and is equal to one-half the difference between the second and third ionization potential of In. The energy for reaction (1) equals $U = U_{\text{latt}} + U_{\text{Coul}}$. The most striking result of Table I is that for reasonable

TABLE I. Calculated values (in eV's) for the energy changes $q\Delta\phi$, $q\Delta\phi_A$, W_D^{St} , and W_A^{St} of Eq. (3c) for In in PbTe. For definition of U_{latt} and U_{Coul} see text. The final column U which is the algebraic sum of U_{latt} and U_{Coul} gives the estimated value for the energy of reaction for the process of Eq. (1). The values for the various energies for the first row are based on the assumption that the repulsive interaction parameter between In and Te ions is the same as for Pb and Te ions. The values for the second row are based on different values for ρ for In^+ and In^{3+} (see text).

	$q\Delta\phi_D$	$q\Delta\phi_A$	W_D^{St}	W_A^{St}	U_{latt}	U_{Coul}	U
$\rho=0.38 \text{ \AA}$	-22.9	18.7	0.2	0.7	-3.3	4.6	1.3
$\rho=0.34 \text{ \AA} (\text{In}^{3+})$	-23.9	18.7	0.1	0.5	-4.6	4.6	0
$0.36 \text{ \AA} (\text{In}^+)$							

values of the repulsion parameter ρ , $U_{\text{latt}} \approx U_{\text{Coul}}$ so that U is much smaller than U_{Coul} . For a particular value of ρ we find $U=0$, indicating incipient negative- U -center behavior. Clearly, slight changes in this or other parameters would lead to a clear-out prediction of such behavior but the important result is that $U_{\text{latt}} \approx U_{\text{Coul}}$, indicating a tendency toward such behavior. The same conclusion can be drawn from the results for the other Group III elements treated in Ref. 12, namely, Al, Ga, and Tl. We chose to display the results for In since evidence toward self-compensation for this impurity in PbTe based systems exists^{6,7} though other workers disagree with that conclusion.¹³ In agreement with our qualitative arguments we see that the tendency toward self-

compensation ($U_{\text{latt}} < 0$) arises from a greater gain $q\Delta\phi_D$ for the donor state (column 1 of Table II) compared with the loss $q\Delta\phi_A$ for the acceptor state (column 2).

We conclude with the comment that having demonstrated the tendency toward negative- U -center behavior of multivalent impurities in an ionic host lattice of the type $A^{2+}B^{2-}$ one is inclined to expect similar behavior in other ionic host crystals. One may even expect a similar tendency in conventional semiconductors with a partially ionic character, such as II-VI compounds.

We greatly appreciate stimulating discussions on this subject with Dr. M. Sturge.

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