Valence-skipping compounds as positive-U electronic systems

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We find that arguments favoring negative-U behavior of *intra-atomic origin*, based upon valence skipping for compounds of column III, IV, and V metals, do not stand up to closer examination. It is suggested that real negative-U behavior (disproportionation in compounds such as $TlBr_2$, Pb_2O_3, and $BaBiO_3$) can, and does, only arise through relaxation of neighbors associated with changes in bond populations. Even then, very high dielectric constants are required to reduce the positive-U contribution, and disproportionation is not expected with lighter metals. Analogous displacements of water molecules may produce disproportionation in aqueous solutions of $TlBr_2$. We find that Tl impurities in PbTe also disproportionate, through atomic displacements with transfer of electrons between bonds, which could explain, as well as would an atomic-electronic origin, an apparent "charge-Kondo effect" behavior, and enhanced superconductivity, found by Matsushita, Blume, Geballe, and Fisher.

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It has long been known that many elements such as Tl, Pb, and Bi can appear in compounds with two different valences, but skip the forbidden valence between. This defines valence skipping, and actually applies to most simple metals. It has further been noted that when one of these forbidden valences appears to arise, as in the forbidden formal valence of three for Pb in Pb_2O_3, there are two inequivalent Pb sites, which may be identified with the allowed two, and the allowed four, valence. This defines negative-U behavior since it indicates that if a pair of such atoms had the "forbidden valence" they would disproportionate so that one gave up its electron and the other took it, as if the usual positive U repulsive energy were replaced by a negative attractive U.

It has perhaps been natural to regard this negative-U behavior as an intrinsic electronic feature of the metallic atoms involved, and a number of workers[1–6] have proceeded with that point of view. Here we examine the arguments which have been used to support this view of an intra-atomic electronic origin. We find that they fail and that the related properties appear to be directly understandable in terms of the tradition concepts of electronic structure, using PbTe and related systems as our examples. The negative-U behavior of some valence skippers is unquestionably there but we argue that it arises from atomic relaxations, the traditional origin of negative-U behavior as in semiconductor defects. The subject is important because such a negative-U Anderson model[7] in compounds can lead to[5] heavy-fermion behavior, a charge-Kondo effect, and can have an insulating—or a superconducting[4,8–11]—ground state. Taraphder and Coleman[5] have argued that these effects are intrinsic to negative-U behavior and independent of its origin, but to estimate the magnitudes of the basic parameters which enter it may be essential to correctly understand the ultimate cause of the negative-U behavior.

Early support for intra-atomic origins of negative-U behavior was given by Varma.[4] One associates the increase in energy required to remove an electron from the atom, as one increases the state of ionization before removal, as arising from the Coulomb repulsion U between pairs of electrons. Listing the successive experimental ionization energies of lead (first neutral Pb, then Pb^+, etc.) from the CRC

Handbook,[12] 0.742, 15.03, 31.93, 42.31, and 68.8 eV, he noted that the difference in ionization energy of Pb^{2+} and Pb^{3+} (the "forbidden valence") was only 10.4 eV, while the differences preceding and following it are 16.9 and 26.5 eV. However, the principal reason for this is that for the preceding set the first was removal of a *p* electron, rather than an *s* electron, and for the following set the first was a removal energy of an *s* electron rather than a *d*-core electron. These differences are 3.0 and 20.8 eV, if taken from Hartree-Fock term values,[13] close to the various estimates which could be obtained from experiment, and the rest of the difference is consistent with small differences in the positive U's between different orbitals. This shows first that the low value for the U which Varma defined does not have anything to do with high correlation energy for closed shells as suggested, but more importantly that the simplest positive-U picture describes these valence skippers very well.

A second atomic motivation for negative U's (Ref. 4) was based upon "stable closed-shell configurations." This is most familiar in the rare earths where the number of *f* electrons increases by one for each step in atomic number until europium, which increases by two to complete the shell (of electrons of a single spin orientation). This is, however, due to the exchange energies of six electrons lowering the energy of the seventh, in comparison to the next step (terbium) where the added *f* electron sees no electrons of the same spin. Even there the exchange is a small effect which favors a local *f* level over an *s* level of nearly the same energy. It does not lead to disproportionation of europium with some having seven and some five *f* electrons, which would correspond to a negative U, nor does it have to do with correlation effects. Exchange does not come up in any case with the single *s* orbital in the compounds of valence III, IV, and V.

A third point[4] concerned the strong screening of these high formal charged states, such as +2 or +4 for Pb. We agree that in the solid these charges are drastically reduced, particularly by the admixture of empty orbitals on the metal to the occupied states of its neighbor atoms. The Coulomb U which is involved is quite different from that which might cause disproportionation. It is the intra-atomic U of, for example, Te atoms in PbTe, which raises the energy of one Te

p orbital when another is occupied by an electron from Pb. It was determined as 8.00 eV from the atomic spectra in Ref. 14, p. 9. If one includes this term in the solid, one must also include the sum of the electrostatic potentials at each Te atom from all the other atoms present, the Madelung energy $-\alpha Z e^2/d$ if Z is the charge on the Pb atoms (e.g., Ref. 14, p. 331, with $\alpha=1.75$ for the rocksalt structure). This is $-7.80Z$ eV for the spacing $d=3.23$ Å of PbTe so the sum is an "effective" $U^* = U - \alpha e^2/d = 0.2$ eV, essentially zero. In some cases the same subtraction may even give a negative value because the Madelung value is an overestimate; the metal (Pb) orbitals overlap the nonmetal (Te) orbitals. Even a negative U^* would not be a cause for instability, and would only effect small changes in the band gap. It still requires the energy of the gap to transfer an electron to a different state. The familiar message (e.g., Ref. 14) is that the formal transfer of electrons between atomic states involves large energies, but only subtle rearrangements of charge. This is no cause for instability, only a finding that it is often reasonable in the solid to use the unshifted term values in simple electronic-structure calculations.

In the context of this small U^* all the properties, and compound formation in particular, are consistent with the traditional simple view. For PbTe in the rocksalt structure with the Pb p-state energy[13] $\varepsilon_p(\text{Pb})=-6.53$ eV, higher than the p-state energy $\varepsilon_p(\text{Te})=-9.54$ eV both p electrons can be transferred from Pb to Te, contributing about 3 eV each to the cohesion per atom pair.[14] With the $\varepsilon_s(\text{Pb})=-12.49$ eV lower in energy than the Te p state, no further electrons can be transferred. Only for oxygen in column VI of the periodic table is the p-state energy[13] $\varepsilon_p(\text{O})=-16.77$ eV lower than the s-state energy for Pb, allowing the possibility of all four electrons being transferred in PbO_2. (Actually Pb_2O_3 also forms[15] with Pb having a *formal* valence of three, to which we shall return.)

A different effective U_{eff} in such a solid has relevance to disproportionation. It is the change in energy in transferring an electron between two Pb sites, or more importantly two Tl impurity atoms in PbTe. The self-consistent-field estimate of this U_{eff} is obtained as for U^*, but the Madelung term now becomes only $-e^2/r$ with the distance r between Tl atoms, larger than the nearest-neighbor d, and the Madelung constant is reduced to one, making the sum of the two terms near U and strongly positive. The term $-e^2/r$ should be reduced by the dielectric constant of the medium, huge for PbTe, but so also should the intra-atomic U term [the potential from a second of two interacting electrons in an atomic cell is reduced by a factor $1/\varepsilon$ from the polarization of all the bonds, or displacement of atoms, outside that cell; e.g., Ref. 14, 207ff]. Thus a reasonable estimate of this U_{eff} is U/ε, but never negative since the static dielectric constant must be positive if a system is to be stable.

An attempt to postulate a system where linear screening changed the sign was made in an early paper by Moizhes and Suprun,[3] who proposed a model in which a negative U_{eff} was thought to arise from electronic effects alone. They imagined atoms with a positive Coulomb U imbedded in spherical cavities of radius r_0 in a medium with dielectric constant of ε. It is an elementary electrostatic calculation to show that putting two electrons on one such atom, with none on

another atom, is higher in energy than putting them on separate atoms by

$$U_{\text{eff}} = U - (\varepsilon - 1)e^2/(r_0\varepsilon). \qquad (1)$$

(They took the two sites far apart and neglected interaction between them.) They argued that if r_0 were small enough, a negative U_{eff} is obtained. That cannot, however, happen in a self-consistent-field theory where the minimum U would be e^2/r for a spherical shell of radius r, which must, however, fit in the cavity so $r < r_0$. This would again seem to rule out a negative U_{eff} in a real system since self-consistent-field theory gives U values quite close to experiment. It would seem quite unrealistic to assume that some correlation energy arises in this case to invert the behavior, but does not show up in analogous systems which have been treated by standard approaches and compared with experiment.

Drabkin, Moizhes, and Suprun[16] also discussed a model including ionic displacements, but taking the dielectric view, as in Ref. 3, using a static dielectric constant, ε_0, rather than the purely electronic one, ε_∞. We would not rule out such a model, but it seems to have the same difficulty as the electronic argument. If one takes the attraction to a central site to be $-e^2/d$ (a force $F_0 = -e^2/d^2$ in the calculation from the next paragraph), one finds the energy gain equal to about half of $-e^2/d$ ($\delta d/d$) for each neighbor with δd the shift in distance due to changing the charge. As in the purely electronic case we expect U to be much larger than e^2/d so even with $X=6$ neighbors we expect $-(X\delta d/2d)\, e^2/d$ to be much smaller than U.

Perhaps a quantitative study of one case where negative U_{eff}'s can occur, though not from intra-atomic correlations, would be helpful. We imagine a Tl substituted for Pb in PbTe, leaving the Tl initially in the "forbidden" valence of 2+. We can define some generalized coordinate x describing the displacement of atoms around this site, with $x=0$ at equilibrium and with a spring constant κ_s stabilizing the structure with an energy $\frac{1}{2}\kappa_s x^2$. Adding or removing an electron from a bond or antibond state will modify the interatomic forces, introducing a term in the energy $F_0 x$. [The simple physical analogue is placing weights of mass M on a dish hung by a spring. Then x is the downward displacement of the dish and $F_0 = Mg$ with g the gravitational constant.] Relaxation to the minimum energy will lower the energy by $-F_0^2/2\kappa_s$. If an electron is taken from one site (giving a term $-F_0 x$ and no s electrons left on that atom) and added to another equivalent site (giving $+F_0 x$ and both s states occupied on that atom), the total gain is $-F_0^2/\kappa_s$. This pairing up, or disproportionation, is always favored unless an extra Coulomb energy U_{eff} for having two on the same site exceeds the difference of $-F_0^2/\kappa_s$. There are no restrictions on the relative magnitudes of the parameters so $U_{\text{eff}} - F_0^2/\kappa_s$ can be negative, not limited by the e^2/r_0 restrictions for Coulomb forces. In fact the F_0 introduced by adding an electron are of the order of eV per Å, and the κ_s, estimated either from the electronic structure (e.g., Ref. 14, p. 87) or by fitting the bulk modulus, are of order eV/Å^2 per neighbor, so the energy gains are of order $1/6$ eV; in this case our estimate is[17] 0.082 eV. It is not reduced by a dielectric constant. The Coulomb $U_{\text{eff}} = U/\varepsilon$ with $U=6.30$ eV for Tl (Ref. 14) and ε equal to 400 or

greater[18] is much smaller, so the disproportionation is expected for Tl impurities in PbTe.

This same picture describes negative-U disproportionation in pure materials. The structures are not so simple but we may generalize from the PbTe(Tl) just described to TlTe in a rocksalt structure, with every lead replaced, and every Tl with the forbidden valence. Then with disproportionation a Tl^{3+} atom attracts neighbors and its neighboring Tl^{1+} repels them, so the elastic term in the energy should be reduced by a factor of order two, doubling the energy gain to some 0.16 eV per Tl^{3+}. Still, with U=6.3 eV we need a dielectric constant of greater than 40 to allow disproportionation. Such constants do arise in the compounds of the Tl row (e.g., PbTe)[18] so disproportionation is likely. $TlBr_2$ indeed occurs in a structure with two inequivalent Tl sites,[15] one Tl^{3+} surrounded closely by four bromine atoms, and the other Tl^{1+} site well removed from the Br tetrahedra, forming an insulating compound, $Tl^+ TlBr_4^-$. Similarly, in Pb_2O_3, there are two distinct Pb sites,[19] one tetravalent with closely spaced oxygen neighbors and one divalent with much more distant oxygen neighbors. Also the compound $BaBiO_3$ is in such a crystal structure[20] having a pentavalent Bi^{5+} site with an octahedron of O-atoms at 2.12 Å and a Bi^{3+} site with an octahedron at 2.28 Å from the Bi^{3+}, again an insulating state. This is traditional negative-U behavior.

We should not expect it in compounds of In, Sn, and Sb and the lighter metals unless they show such large dielectric constants. These metals will be valence skipping, but may not show negative-U disproportionation. For example, if we brought atoms together to form a Ca_2O crystal, we would gain energy by the transfer of electrons to the oxygen, but would leave forbidden Ca^+ ions. We would not expect the dielectric constant to be sufficient [ε_0 is 11 in CaO, and[14] U(Ca)=6.60 eV] to allow disproportionation, but we would certainly gain energy by removing half the Ca as neutral atoms, forming a lump of Ca metal and leaving CaO behind. Ca_2O, and compounds of other light metals with formal forbidden valences, simply do not form.

How does one then understand $TlBr_2$ dissolved in water, where the Tl ions appear as half Tl^{1+} and half Tl^{3+}. Any model based upon the polarizability of the water molecules, or their extra attraction to a triply charged ion, seems to require unreasonably small U values in comparison to the required attraction, for the reasons given before. There is a new effect arising from the aligning of the molecular dipoles around the charged ions, but for a water molecular dipole of 0.39 eÅ, the coupling is so strong that all neighbors are fully aligned at room temperature for single charges, and negligible energy is gained by disproportionation. On the other hand, there is no reason why the removal of both s electrons from a Tl, eliminating the principal repulsion which holds the water molecules out from the ion, might not gain energy in excess of the intra-atomic U_{eff}, as in the $TlBr_2$ discussed above. There is no apparent relation between the magnitudes of the competing effects, and it would be a disproportionation resulting from molecular displacements.

We consider finally Ref. 6 which gives convincing evidence of a Kondo-like rise in resistance at low temperatures, without magnetic-field dependence. This indicates a negative-U source as in Ref. 5, rather than a local moment. The authors therefore suggested the charge-Kondo effect based upon disproportionation as an explanation, making reference to the papers (e.g., Ref. 4) we have described. We noted that Taraphder and Coleman[5] have indicated that the behavior is independent of the origins of the interaction, so our finding of disproportionation of the Tl impurities in PbTe, is in support of the conjecture by Matsushita, *et al.*[6] On the other hand, an essential term in the negative-U Anderson model[5,7] is the coupling $Vc_{\mathbf{k}\sigma}^+ d_{j\sigma} e^{-i\mathbf{k}\cdot\mathbf{R}_j}+\text{H.c.}$ If the value of the configuration coordinate x differs by δx between the two coupled electronic states, the coupling is reduced by the familiar Debye-Waller factor, $\int \varphi_0(x-\delta x)\varphi_0(x)dx = \exp(-\frac{1}{8}(\delta x/a_0)^2)$ (e.g., Ref. 21, p. 310), with φ_0 the ground-state harmonic oscillator wave function and a_0 the zero-point fluctuation (e.g., Ref. 21, p. 41; the mass which enters here is six times the Te mass since six neighbors move). For our parameters[17] $a_0=0.0124$ Å and this factor is 0.093, weaking but not eliminating the contribution to the Kondo scattering and to superconductivity. The corresponding distortions in PbTe(Tl) have not been observed, but our small estimate of[17] $\delta x=\pm 0.05$ Å might be difficult to detect.

We conclude that none of the arguments we could find, which have been used to suggest an intrinsic atomic origin for negative-U behavior of some metals, survive a closer look, and estimates of the relevant parameters argue against it. It is therefore reasonable to abandon this prevalent view and look to other sources, such as traditional lattice relaxation, for the observed behavior.

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