

## Configurational energies of high-valence impurities dissolved in metals\*

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The energies for various ionic configurations of high-valence impurities in simple metals are deduced empirically and compared with the predictions of a simple model of impurity structure. The possibility that configurations other than the ground state are optically accessible is discussed.

In recent papers<sup>1,2</sup> we have reported properties of higher-valence impurities in monovalent metallic host lattices. Suitable impurities, such as the halogens, form charge-transfer complexes in which the negatively charged halogen ion is screened by repelled band states. The purpose of this addendum is to deduce, and to illustrate using a simple model, the energetics of the charge-transfer process, and to draw attention to the probable existence of optically accessible excited charge-transfer states.

Consider first the energies required to introduce halogens into solution in liquid alkali-metal hosts as negative ions. These can be deduced from studies of the solubility of salts in the molten alkali metals.<sup>3</sup> We employ a cycle in which the salt is first broken into ions at expense of energy  $E_S$ , the cohesive energy of the salt. An electron is then transferred from each halogen to an alkali atom, requiring energy  $\alpha_H - \mathcal{I}_A$ , with  $\alpha_H$  the halogen affinity and  $\mathcal{I}_A$  the alkali ionization potential. The alkali atom, when placed in solution, releases the cohesive energy  $E_c$  of the alkali metal, and the halogen requires the desired energy of ground-state solution  $E^-$ . These energies add to give the observed energy of solution of the alkali halide  $E_{AH}$ . Thus

$$E^- = E_{AH} - \alpha_H + \mathcal{I}_A - E_S + E_c . \quad (1)$$

Although the energies  $E^0$  to dissolve halogens as neutral atoms, rather than ions, are not known experimentally, they can be estimated with adequate precision from the properties of noble gases in solution. In the four cases known to the author, the energies of solution of noble gases in the liquid alkalis are LiHe,<sup>4</sup> 0.014 Ry; KHe,<sup>4</sup> 0.023 Ry; NaAr,<sup>5</sup> 0.051 Ry; NaXe,<sup>6</sup> 0.008 Ry. These are probably just energies  $\sim 0.04$  Ry to make the hole for the dissolved atom, modified somewhat by dispersion interaction between the inserted atom and the host. To within the required accuracy of a few hundredths of a rydberg the energy may be taken as 0.03 Ry. Since chemical properties are not involved, we can expect much the same energy change  $E^0 \approx 0.03$  Ry when neutral halogen or

chalcogen atoms occupy a hole in alkali lattices, and this estimate will be used in what follows:

Consider now the energy  $E^+$  required to insert positive ions of these impurities into solution, with one electron contributed to the conduction band. For this case, also, no direct experimental data are available, but the required energy can be estimated very simply and accurately. The point is that S\* ( $3s^2 3p^3 4s$ ), Cl\* ( $3s^2 3p^4 4s$ ), Ar\* ( $3s^2 3p^5 4s$ ), and K ( $3s^2 3p^6 4s$ ), for example, have almost identical valence structures. The  $4s$  one-electron energies are 0.282, 0.301, 0.310, and 0.319 Ry in the four cases.<sup>7</sup> Differences among these binding energies are much less than those among the different alkali metals; and, since the energies of intersolution among alkali metals are  $\sim 0.001$  Ry,<sup>8</sup> it follows that the energy required to put excited Ar into an alkali metal is just  $-E_c$ , with  $E_c$  the cohesive energy of K. We therefore find

$$E^+ = \mathcal{I} - \mathcal{I}^* - E_c , \quad (2)$$

with  $\mathcal{I}$  and  $\mathcal{I}^*$  the ionization potentials of the ground and excited states of the free impurity atoms. This prescription should be accurate to within 0.01 Ry.

Figure 1 shows the absolute thermal energies  $E^+$ ,  $E^0$ , and  $E^-$  deduced in this way for Xe, I, and Te in Na. The energy of  $\text{Te}^{2-}$  was obtained using the observed energy of  $\text{Na}_2\text{Te}$ , together with an estimate of 0.01 Ry for the heat of solution, obtained from the phase diagram.<sup>9</sup> The energy of  $\text{Te}^-$  was determined by setting  $E^0 - E^-$  equal to that for I, apart from a small correction for the dissimilar affinities. The results show clearly that  $\text{Xe}^0$ ,  $\text{I}^-$ , and  $\text{Te}^{2-}$  are the stable states. Similar analyses may be performed for impurities occupying other rows of the period table, and other host lattices.

The arguments given above already reveal the origins of the energies  $E^+$  and  $E^0$ . This is not the case for  $E^-$  and  $E^{2-}$ , which are derived quite empirically. We shall therefore present a simple model that incorporates the important features of the charge-transfer processes (0) - (-) - (2 -), etc.

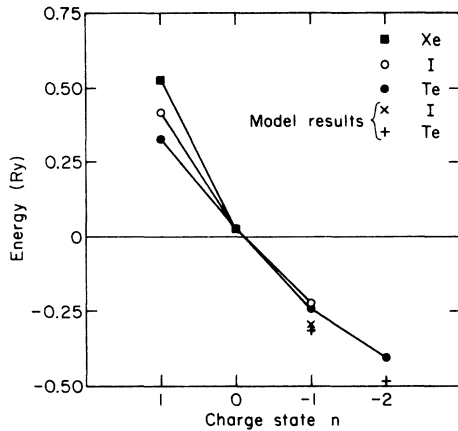


FIG. 1. Absolute energy, with respect to the free impurity atom and pure metal, of Xe, I, and Te, for various ionic configurations in Na. Crosses show predictions of the simple model discussed in the text.

We shall neglect impurity-conduction band-exchange and core-core overlap interactions by assuming that the impurity is isolated in the Coulomb hole of the lattice, so that the impurity and host only interact electrostatically. With a square hole in the electron-gas density, displacing the required  $n+1$  electrons from the neighborhood of the impurity of net charge  $-n|e|$ , the potential at the impurity site due to the surrounding lattice is

$$V_n = (3|e|/2r_s)[(n+1)^{2/3} - 1], \quad (3)$$

with  $r_s$  the cell radius in a monovalent electron gas. The work required to transfer an electron from the electron gas to an impurity with initial charge  $-(n-1)|e|$  is then given in terms of the host work function  $W$  by

$$W_n = W - \alpha_n - (9e^2/10r_s)B_n, \quad (4)$$

with

$$B_n = (n+1)^{5/3} - n^{5/3} - \frac{5}{3}. \quad (5a)$$

To improve on this crude model we recognize that the edges of the Coulomb hole must be blurred over a distance  $k_F^{-1}$ , thereby adding to the potential at the origin. However, the effect is quite small, the potential being  $\sim 0.1e/r_s$ , and we shall presume that this dipole layer merely cancels the dipole layer at the crystal boundary, which has also been neglected. In addition, the kinetic energy of the electron gas is modified by scattering at the central impurity. For macroscopic boundaries this effect is the major source of surface free energy  $\gamma$  of the metal. By parametrizing the electronic kinetic energy in terms of the surface energy we now recover Eq. (4), but with

$$B_n = (n+1)^{2/3}(n+1-\beta) - n^{2/3}(n-\beta) - \frac{5}{3}, \quad (5b)$$

and

$$\beta = 40\pi\gamma r_s^3/9e^2 = 0.117 \pm 0.01 \quad (6)$$

for the alkali metals. The valence energy levels of the impurity consistent with the potential given by Eq. (3) are

$$E_n = -\alpha_n - \frac{3e^2}{2r_s} [(n+1)^{2/3} - 1]. \quad (7)$$

Let us first examine the one-electron levels given by Eq. (7). Figure 2 shows as crosses the  $E_n$  calculated using standard affinities and  $r_s$  for Xe, I, and  $\text{Te}^{2-}$  in K. The values are, in addition, spin-orbit averaged. Also shown in Fig. 2, as open circles, are theoretical Hartree-Fock energies<sup>2</sup> obtained for these cores when coupled self-consistently to the random-phase-approximation (RPA) response of the host-electron gas. Clearly, Eq. (7) reproduces the major trends of the detailed calculation. For Xe and I the simple model yields lower energies. This is just what should happen, because the  $\alpha_n$  include  $5p$  correlation energies  $\geq 0.1$  Ry omitted from the HF scheme. The trend is broken for  $\text{Te}^{2-}$ , probably because the valence orbitals spread in the wide Coulomb well. Figure 2 suggests that  $\alpha_2$  for Te should be taken as  $\sim -0.45$  Ry under these circumstances, rather than the value  $-0.574$  Ry derived from studies of

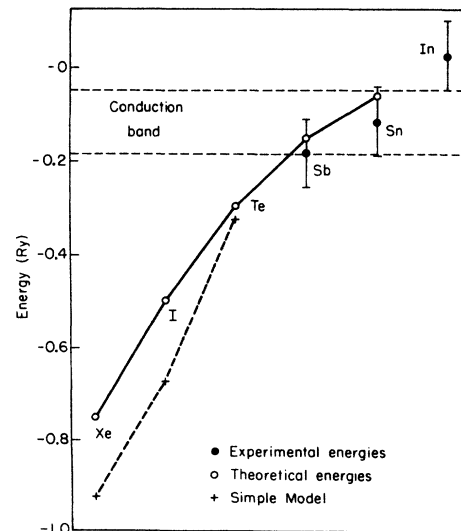


FIG. 2. One-electron spin-orbit-averaged energies of outer valence  $p$  states for group 5 impurities in K. Open circles are HF results for cores coupled self-consistently to the electron gas, and crosses show predictions of the simple model, including Coulomb correlations. The solid circles are values with respect to the K conduction band, deduced from experiment.

TABLE I. Comparison of deduced thermal charge-transfer energies  $E^- - E^0$  with predictions  $W_1$  of simple model for halogens in alkali metals (values given in rydbergs).

Metal halogen	Na				K		Cs		
	F	Cl	Br	I	F	Cl	F	Cl	I
$-(E^- - E^0)$	0.44	0.38	0.32	0.25	0.46	0.38	0.48	0.39	0.33
$-W_1$	0.34	0.35	0.33	0.32	0.31	0.32	0.30	0.31	0.28

the more restricted Madelung well in salts.<sup>10</sup> For halogens, of course, the ions are bound even in free space, and this effect may be negligible.

We can now apply Eq. (4) to the prediction of charge-transfer energies. Results obtained in this way are compared in Table I with the thermal charge-transfer energies  $E^- - E^0$  calculated above. There is satisfactory general agreement between  $E^- - E^0$  and the energy  $W_1$  predicted from the simple model, for large ions in solution but not for small ions such as F. The discrepancies vary systematically with halogen species and undoubtedly originate in lattice relaxation, which draws neighboring positive solvent ions close to small negatively charged impurities, thereby deepening the potential well. These effects are included in the observed heats of solution, but are omitted from the simplified model.

Equation (4) may also be applied to the second-ionization process. For Te in Na one finds  $W_2 = -0.18$  Ry for the Te affinity as modified above, in good accord with the result  $-0.15$  Ry for  $E^{2-} - E^-$  presented in Fig. 1. Charge-transfer energies derived in this way have been employed to obtain absolute values of  $E^-$  for I and  $E^{2-}$  for Te, using the result  $E^0 = 0.03$  Ry. These energies, shown as "model results" in Fig. 1, provide a very satisfactory account of the energies derived from thermal data. It is interesting to note that Eq. (4) gives  $W_2 = 0.02$  Ry for Te in Cs, so that

$Te^{2-}$  is mildly unstable in Cs. However, lattice relaxation of the widely spaced Cs atoms may stabilize the  $n = -2$  state. The degree to which different ionic configurations hybridize when nearly degenerate is, of course, not yet known.

We have seen in the preceding paragraphs that the evidence strongly supports a belief that high-valence impurities adopt ionic ground-state configurations in metals. It is now natural to inquire whether ionicities other than the ground state have any significance as states of the composite host-impurity system. The answer is very likely to be affirmative. Indeed, it seems quite probable that optically induced charge-transfer transitions may carry the system from the ground state to configurations of different ionicity. The charge-transfer process is simply the trapping of an electron-hole pair at the impurity. In the case of an  $n = 1$  to  $n = 0$  transition, for example, a core hole and a band electron are bound to the impurity. This configuration must appear as an electron-hole resonance in the excitation spectrum of the crystal. For  $p$  core states, transitions of this type should possess substantial oscillator strengths. In this respect it is interesting to note that the thermal charge-transfer energies of halogens in alkali metals, when augmented by the elimination of lattice-relaxation terms, must fall in energy ranges quite comparable to those of first exciton lines of the analogous salts.<sup>11</sup>

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