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Comments and Addenda

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Electron energies of ions in crystals

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The energies of photoemitted electrons are calculated for alkali halide and alkaline-earth chalcogenide crystals. The ionization energy of the closed-shell ions are calculated in the crystalline environment, which is simulated as a spherical average of pseudopotentials. Apparent binding energies in photoemission are obtained by adding these ionization energies to the hole self-energies from electronic relaxation.

In a photoemission experiment, the electron exits from the solid and leaves a hole behind. In ionic solids, in most cases, experiments show that the hole is localized.[1-3] When the hole is localized, the energy of the photoemitted electron can be calculated from the ionization energy of the ion, added to the self-energy of the hole from electronic relaxation.[1-4] As we showed earlier, the peak in the photoemitted energy distribution is given by this electronic contribution to the hole energy.[4] The phonon contribution does not affect the peak position since the electron departs too rapidly for the slow-moving ions. The phonon contribution does affect the width of the peak, and we showed that this seemed well described by the hole-phonon interaction.

In an earlier paper,[4] we reexamined the hole self-energy terms in the localized-hole-point-ion (LHPI) model, and found one term which had been overlooked by prior workers in this field. This term, which we called Σ_2, when added to the traditional terms of Madelung and Mott-Littleton,[5] gave rather good agreement with experimental photoemission binding energies in the alkali halides. The only parameters which enter into this theory are the ionization energies and polarizabilities of the free ions.

Here we wish to redo this calculation, and to consider three new points: (1) Recently we reevaluated the polarizability of ions in crystals[6] and produced a new set of crystal polarizabilities for the alkali-halide and alkaline-earth chalcogenides. Their characteristic is that the cation polarizability is constant, while the anion polarizability depends linearly upon inverse lattice constant. Thus we wish to use our own polarizabilities in calculating the hole self-energies. In some cases, our polarizabilities cause energy shifts of 0.5 eV from the energies found using other polarizability sets. (2) We present a calculation of the repulsive energy E_R. It is defined as the change in the energy of the photoemitted electron due to the change in the repulsive energy of the ion containing the hole. Citrin and Thomas[1] originally argued that this was a substantial correction, on the order of one electron volt. We had argued[4] that it was negligible. Our present results show that each side was half-right. The repulsive energy is entirely negligible for electrons originating from cations, but for electrons from anions, the repulsive energy is indeed a sizable fraction of an electron volt. (3) We wish also to perform the same calculations on the alkaline-earth chalcogenides.

I. BINDING ENERGY

In the LHPI model, the apparent binding energy E_b of an electron originating from an anion (A^-) or cation (C^+) site is given by the formulas

$$\begin{aligned} E_b(A^-) &= E_{IP}^0 + E_M - E_R - \Sigma_{\rm ML} - \Sigma_2\,, \\ E_b(C^+) &= E_{IP}^0 - E_M - E_R - \Sigma_{\rm ML} - \Sigma_2\,, \end{aligned} \tag{1}$$

where E_M is the Madelung energy, E_{IP}^0 is the ionization energy of the free ion, $\Sigma_{\rm ML}$ is the hole self-energy of Mott and Littleton, and Σ_2 is the additional hole self-energy given in Ref. 4. In order to avoid confusion in signs, all symbols refer to positive quantities except Σ_2 whose sign varies from case to case. For values of the ionization energy E^0_{IP} of the free ion, we can either use experimental values or our theoretical ones, which are very similar. The Madelung energy is just the Madelung constant times e^2/a. The calculation of Σ_{ML} and Σ_2 requires only a knowledge of the lattice constant and polarizability. Our new set of polarizabilities is shown in Table I. The values of Σ_{ML} and Σ_2 obtained from them are shown in Tables II and III. These values, particularly Σ_2, vary about 0.2–0.4 eV from our earlier values obtained using the polarizabilities of Tessman, Kahn, and Shockley (TKS).[7]

II. IONIZATION ENERGY

Table IV shows our calculated ionization energies of free ions. They were obtained by following the method of Bryant,[8,9] whose theoretical values were nearly identical. The eigenvalues and wave function of the ions are obtained in the local density approximation. The total energy of the ion is calculated both for the closed shell and with a hole in the p shell, and the ionization energy is the difference between these two values. We also employ the self-interaction correction, which was pioneered by Bryant. It makes negative ions stable, and provides an accurate calculation of their ionization energy or electron affinity.

There is good agreement between theory and experiment for the free-ion results in Table IV. Our calculational accuracy is about +0.002 Ry which is obtained by varying the step size of the integration, etc. However, for higher atomic numbers, our values are certainly less accurate than that for two reasons. The first is that our calculation is nonrelativistic, and the inner states of heavier ions need a relativistic description. Second, for large Z the total ground-state energy of an ion becomes a very large number and the ionization energy is the small difference between two very large numbers. So at large Z one has the problem of the number of significant digits in the computation. For these reasons we do not present results for the $5p$-shell ions and the error uncertainty in the $4p$-shell series is probably ±0.01 Ry unit. We were unable to find an experimental value for the ionization energy of Sr^{2+}. The double-negative ions are not stable as free ions, so no values are given.

TABLE I. Dipole polarizabilities (Å^3).[a]

	Cation	F^-	Cl^-	Br^-
Li^+	0.030	0.89	2.94	4.13
Na^+	0.14	1.02	3.15	4.78
K^+	0.96	1.05	3.21	4.39
Rb^+	1.50	1.05	3.31	4.44
	Cation	O^{2-}	S^{2-}	Se^{2-}
Mg^{2+}	0.063	1.73	4.82	5.94
Ca^{2+}	0.67	2.27	5.33	6.50
Sr^{2+}	1.19	2.35	5.76	7.03
Ba^{2+}	2.00	2.48	5.87	7.48

[a] G. D. Mahan, Solid State Ionics 1, 29 (1980).

III. REPULSIVE ENERGY

The repulsive energy is calculated in the following fashion. We calculate the ionization energy of the closed-shell ion in the crystalline environment. As described elsewhere,[6] the crystalline environment is taken to be a spherical average of pseudopotentials. The ionization energy one calculates in this case is

$$E_{IP}(A^-) = E^0_{IP} + E_M - E_R\,,$$

$$E_{IP}(C^+) = E^0_{IP} - \Sigma_M - E_R\,.$$

The ionization potential in the crystal must first be corrected for the Madelung energy, due to the charges on the surrounding ions. Table IV lists our results for ionization energies, as corrected for only the Madelung potential; we list $E_{IP} + E_M$ for cations and $E_{IP} - E_M$ for anions. If there were no repulsive energy, this quantity would equal the calculated value E^0_{IP} of the ionization energy of the free ion. Any difference between these entries is due to the repulsive energy term E_R.

The energy E_R represents the following physical process. The central ion containing the core hole changes its effective size (radius) because of the loss of one electron. This contraction lowers the repulsive energy it feels from the neighboring ions. The lowering of repulsive energy imparts additional kinetic energy to the photoemitted electron, which appears as a reduced binding energy E_R. Thus the calculation of E_R describes the relaxation of the central ion. It does not include the relaxation of the neighboring ions, which is included through the self-energy terms Σ_{ML} and Σ_2.

For cations, one can see that the ionization energies in the crystalline environment (after corrections for E_M) are nearly identical to those for the free ions. The differences, which are of order 0.01 Ry, probably represent calculational uncertainties rather than true repulsive energies. Our conclusion is that any repulsive energy, if it exists, is smaller than 0.01 Ry for cations. Earlier we showed[6] that the polarizability of cations

TABLE II. Binding energies (eV): Alkali halides.

				Halide hole				Alkali hole		
Salt	E_M	Σ_2	Σ_{ML}	E_A	$E_b(H^-)$	Expt.	Σ_{ML}	E_A	$E_b(A^+)$	Expt.
LiF	12.529	1.887	1.847	1.78	10.57	12.85	2.973	75.62	58.23	
LiCl	9.812	2.040	1.904	2.68	8.55	10.6	3.179	75.62	60.59	60.7
LiBr	9.149	2.055	1.911	2.24	7.43	9.8	3.216	75.62	61.20	
LiI	8.389	2.040	1.896				3.217	75.62	61.97	
NaF	10.894	1.168	1.480	2.47	10.72	13.4	2.167	47.29	33.06	36.9
NaCl	8.924	1.554	1.576	2.99	8.78	10.4	2.530	47.29	34.28	36.3
NaBr	8.426	1.618	1.598	2.73	7.94	9.2	2.605	47.29	34.64	35.7
NaI	7.776	1.656	1.599				2.647	47.29	35.21	35.5
KF	9.413	0.064	1.693	2.77	10.43	10.9	1.731	31.81	20.60	21.23
KCl	7.998	0.775	1.491	3.09	8.82	9.7	1.969	31.81	21.07	22.5
KBr	7.626	0.939	1.480	2.83	8.03	8.8	2.066	31.81	21.18	21.2
KI	7.123	1.098	1.456				2.151	31.81	21.44	21.0
RbF	8.924	−0.254	1.796	2.88	10.26	10.4	1.641	27.50	17.19	17.6
RbCl	7.648	0.520	1.503				1.825	27.50	17.51	18.4
RbBr	7.343	0.694	1.481				1.916	27.50	17.55	18.0
RbI	6.855	0.884	1.425				1.986	27.50	17.77	18.3

is also insensitive to crystal environment. Apparently the cations can be treated in a Born-Mayer model, in that their properties are really independent of where they are located.

A quite different behavior is found for anions. Earlier we showed that the polarizability depended upon crystalline environment.[6] In the same way, we now find that the ionization energy of anions is dependent upon the crystal. For halide ions, the repulsive energy is as large as $E_R = 0.245 - 0.131 = 0.114$ Ry for F^- in LiF. However, typical values for the other cases are 0.04 to 0.06 Ry, or 0.5 to 1.0 eV. The value of E_R systematically decreases with increasing lattice constant. The difference between anions and cations is mainly that the cations are more tightly bound, and hence less influenced by the crystalline potential.

The chalcogenide ions are a special case of anions. The double-negative ion is not stable in vacuum, but is stabilized by the crystalline potential. Our local density code behaves correctly, in that it finds solutions for the ion in the crystal, but not in vacuum. The ionization energy listed in Table IV is actually the quantity $E_{IP} - E_M$: They are negative because the Madelung energy is larger than the ionization energy. Figure 1 shows the values in Table I plotted versus the inverse lattice constant of the ionic crystal. For each anion there are four points, one each for the four crystals. The rather straight line connecting the points is only meant to guide the eye. The linear behavior of ionization energy versus (a_B/a) is similar to the linear behavior of polarizability versus (a_B/a) reported earlier.[6]

TABLE III. Binding energies (eV): Alkaline-earth chalcogenides.

				Anion			Cation	
Salt	E_M	Σ_2	Σ_{ML}	E_A	$E_b(A^-)$	Σ_{ML}	E_A	$E_b(C^+)$
MgO	23.903	4.954	2.483	−12.93	3.54	4.057	80.10	47.19
MgS	19.346	5.064	2.424	−8.25	3.61	4.116	80.08	51.55
MgSe	18.467	5.008	2.389	−7.19	3.88	4.081	80.09	52.53
CaO	20.925	2.673	2.603	−11.68	3.97	3.496	50.72	23.62
CaS	17.690	3.585	2.292	−7.80	4.01	3.516	50.68	25.89
CaSe	17.032	3.725	2.254	−7.03	4.02	3.537	50.71	25.42
SrO	19.507	1.481	2.556	−11.20	4.27	3.055	42.91	18.87
SrS	16.722	2.839	2.229	−7.50	4.15	3.209	42.88	20.11
SrSe	16.158	3.056	2.190	−6.78	4.13	3.255	42.89	20.42
BaO	18.226	0.460	2.599	−10.75	4.42	2.756	35.48	14.04
BaS	15.759	1.949	2.154	−7.21	4.45	2.830	35.48	14.94
BaSe	15.252	2.314	2.128	−6.53	4.28	2.942	35.48	14.97

TABLE IV. Ionization energies (rydberg).

	Free ion						Free ion				
M	Expt.[a]	Theor.	*M*F	*M*Cl	*M*Br	*A*	Expt.	Theor.	Li*A*	Na*A*	K*A*
Na^+	3.478	3.474	3.481	3.485	3.485	F^-	0.254	0.245	0.131	0.182	0.204
K^+	2.340	2.331	2.310	2.311	2.311	Cl^-	0.265	0.265	0.197	0.220	0.227
Rb^+	2.02	2.008	2.006	2.006	2.004	Br^-	0.247	0.266	0.165	0.201	0.208

	Free ion									
M	Expt.[a]	Theor.	*M*O	*M*S	*M*Se	*A*	Mg*A*	Ca*A*	Sr*A*	Ba*A*
Mg^{2+}	5.893	5.894	5.892	5.890	5.891	$O^=$	−0.951	−0.859	−0.824	−0.791
Ca^{2+}	3.767	3.743	3.731	3.728	3.730	$S^=$	−0.607	−0.574	−0.552	−0.530
Sr^{2+}		3.138	3.156	3.154	3.155	$Se^=$	−0.529	−0.517	−0.494	−0.480

[a] C. E. Moore, *Atomic Energy Levels*, Nat. Stand. Ref. Data Ser. No. 467 (Natl. Bur. Stand., Washington, D.C., 1949).

IV. RESULTS AND DISCUSSION

The ionization energies listed in Table IV are called $E_A = E^0_{IP} - E_R$ and put into Tables II and III. They are combined with the other entries according to Eq. (1), which finally produces the desired values of E_b for holes in cations and anions. A final column in Table II gives the average of experimental values[1-3] for the observed binding energies in alkali halides. There is a systematic difference between theory and experiment in that the theoretical values are too low in magnitude—and predict less binding. This disagreement is in contrast with our earlier findings which had good agreement between theory and experiment for electrons from halide ions. The present calculation reports two improvements in the theory: (1) better polarizabilities, and (2) inclusion of repulsive energies. Both changes tend to worsen the agreement between theory and experiment and in the same direction.

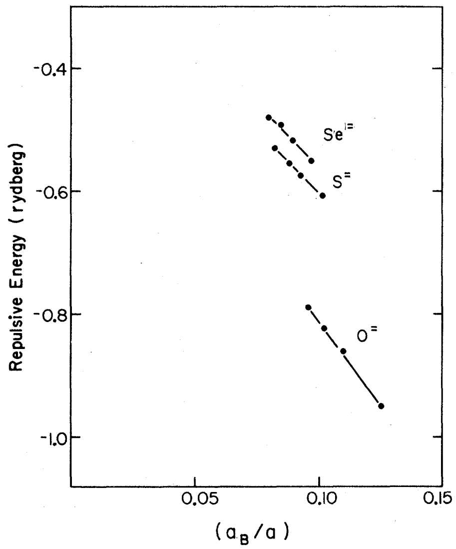

FIG. 1. Repulsive energy of chalcogenide ions in crystals versus the inverse lattice constant. This energy is defined as the theoretical ionization energy minus the Madelung energy. The four points for each anion *A* represent the crystals Mg*A*, Ca*A*, Sr*A*, and Ba*A*. The straight line connecting the points is only meant to guide the eye.

For electrons originating from alkali ions, the present values of E_b are generally smaller by 0.2–0.3 eV than our prior values; the difference is wholly from the change in polarizabilities, since the repulsive energies are negligible. Again there is a systematic disagreement between theory and experiment with the experimental values being larger. This disagreement had been found earlier and has not been altered much by the present results.

In summary, we have tried to do a better job at the theory and have managed to worsen the agreement between theory and experiment. The systematic nature of the disagreement suggests that some important feature of the physics is being overlooked.

Table III shows our calculated binding energies for the alkaline-earth chalcogenides. Experimental data seem available only for MgO. Two different groups[10,11] report the cation binding energy is 50.9 or 51.6 eV below the Fermi level of Mg, which is a much larger binding energy than our value of 47.19 eV from the vacuum. One group[11] showed a valence-band peak at a binding energy of six volts, which again is much more bound than our value of 3.5 eV.

We will rashly speculate that the above disagreements between theory and experiments are caused by uncertainties in the experimental values. This uncertainty is due to the uncertain value of the chemical potential in ionic crystals. As mentioned in Refs. 10 and 11, in interpreting photoemission data from a metal sample, one must account for the difference in work functions of the sample and the spectrometer. The external kinetic energy is measured by retarding voltages (or an equivalent) which is the difference between the chemical potential of sample and spectrometer. In order to renormalize to their difference in vacuum energies, one must subtract their differences in work functions.

In principle, the same subtraction must be done when the sample is an insulator. The problem is that an insulator does not have a known, *a priori*, value of chemical potential. The chemical potential is at an energy which is between the conduction and valence band, but its precise location depends on the impurity content of the sample and will vary from sample to sample. Thus the reported experimental data, both for alkali halides and alkaline-earth chalcogenides, has an arbitrary reference energy (the sample chemical potential) which varies from sample to sample. Its value is not reported and is presumed unknown. I believe that this variation in reference energy for each sample explains the substantial difference (often 2–3 eV) between binding energies reported by different investigators.[1-3] We also are unable to provide a definitive comparison between theory and experiment until such values are known.

ACKNOWLEDGMENTS

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