JOURNAL OF SOLID STATE CHEMISTRY 13, 237–244 (1975)

X-Ray Photoelectron Spectroscopic Studies of Solid Electrolytes

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Received April 6, 1974

A study of solid electrolytes by X-ray photoelectron spectroscopy reveals that silver (I) and copper (I) compounds generally show very small shifts in electron binding energies. The complex crystal structure of the β-aluminas, however, gives rise to different cation sites which can be distinguished by this technique. Calculations of self-potential show the importance of this term for determining shifts. The possibility of determining the partial ionic charge from the measured shift is also considered.

Introduction

It has been suggested that X-ray photoelectron spectroscopy (ESCA) may be able to distinguish between cations in different crystal sites in a lattice (*1–3*). Solid electrolytes are believed to exhibit their high ionic conductivity because of the possibility of the mobile cation being able to occupy different sites in the crystal lattice (*4*). A study of two classes of solid electrolytes has been undertaken and the measured binding energies compared with those exhibited by the same cations in other compounds.

It appears that XPES cannot, in fact, distinguish between different sites in the first series (silver (I) and copper (I) compounds) but this was possible with the second series (β-aluminas).

Subsequently, some calculations were performed to try to explain these two sets of experimental results.

Experimental

The samples were run on an AEI ES100 spectrometer, using either Mg $K\alpha_1\alpha_2$ or Al$K\alpha_1\alpha_2$ radiation. The samples were mounted as finely ground powders on a copper grid to ensure good thermal and electrical contact with the copper sample block. The grid used was of small hole size to minimize differential sample charging and consequent peak broadening (*5*). The samples were calibrated with reference to the gold $4f7/2$ electron peak, with binding energy set at 84.0 eV, by applying a little gold dust to the sample surface. The pressure in the spectrometer was, typically, of the order of 10^{-6} Torr.

Overlapping peaks were resolved with a Dupont model 301 curve resolver using a Gaussian shape fit.

The sample of sodium-β-alumina was from the Harbison Carborundum Company, this was also used to prepare silver and lithium β-alumina. The sodium β''-alumina ($Na_2O \cdot 5Al_2O_3$) came from British Rail. The percentage residual cation in the β-aluminas can be approximately estimated from the intensities of the photoelectron peaks as 8–15% sodium in silver-β-alumina, 6–12% silver and ~5% sodium in lithium-β-alumina.

Results

The binding energies of the silver $3d5/2$ electrons and copper $2p5/2$ electrons were measured above and below the transition temperature for the first series of compounds (Table I). These values were compared to those for a series of silver (I) compounds of

TABLE I

Name of compound	Transition temperature (°C)	Temperature of spectra (°C)	Binding energy (eV)	Coordination of Ag^+ ions
Silver iodide	146	Ambient	368.6	4
		150	368.5	2, 3, 4
Silver rubidium iodide	−155	Ambient	368.9	4
		−160	368.5	
Silver mercuriiodide	50	Ambient	368.7	4
		60	368.6	4
Silver sulphide	179	Ambient	368.7	
		200	368.8	2, 3, 4
Silver selenide	133	Ambient	368.2	
		150	368.2	2, 3, 4
Silver telluride	150	Ambient	369.0	
		180	369.0	3, 4, 6
Cuprous iodide	407[a]	Ambient	933.6	4
Cuprous mercuriiodide	67	Ambient	933.5	4
		80	933.6	4
Cuprous sulphide	91	Ambient	934.3	
		100	934.2	3, 4, 6

[a] The spectrometer is not equipped to heat samples to a temperature >400°C.

TABLE II

Compound	Binding Energy (eV)
Silver fluoride[a]	368.4
Silver bromide[a]	368.0
Silver chloride[a]	368.1
Silver oxide[b]	368.4
Pollard's salt $(NH_4)_6(AuCl)_3Ag_2Cl_5$[c]	368.0
Silver nitrate	368.4
Silver iodate	369.1
Silver perchlorate	368.5
Silver benzoate	368.1
Silver permanganate	367.9
Silver sulphate	368.0
Silver thiocyanate	368.2
Silver orthophosphate	367.9
Silver bromate	369.0
Silver acetate	368.7
Silver metal[d]	368.3

[a] Coordination number of silver ion is six.

[b] Coordination number of silver ion is two.

[c] Coordination number of silver ion is three; the sample was prepared according to (*8*).

[d] Compare value of 368.2 eV (*7*).

varying coordination number and crystal structure (Table II); for the copper (I) compounds they may be compared to those of Ref. (*6*).

Similarly the binding energies of the 1*s*, 2*s*, or 3*d*5/2 electron were measured for the mobile cations in the β-aluminas. In cases where the cation exchange was incomplete, the residual cation electron binding energies were also measured (Table III).

Calculations

The shift in binding energy that occurs between a solid containing atoms of charge $q_c = 0$ and a solid containing atoms of charge $q_c = q_c$ is given by the electrostatic potential model developed by Siegbahn (*10*):

$$\text{Shift} = B_c^{q_c} - B_c{}^0 = \frac{q_c}{r} + \frac{\phi q_c}{R}, \qquad (1)$$

where r = ionic radius, ϕ = Madelung constant or ϕ/R = self-potential, $B_c^{q_c}$ = binding energy of solid of atoms of charge q_c and $B_c{}^0$ = binding energy of solid of atoms of charge 0.

TABLE III

Compound	Cation electron	Binding energy of peaks (eV)		Proportion of major peak (%)
			Major peak	
Sodium-β-alumina	Na2*s*	66.8	64.3	66–83
Hydrated Sodium-β-alumina	Na2*s*	67.0	64.8	80
Sodium-β″-alumina	Na2*s*	—	64.2	100
	Li1*s*	[a]	52.3	[a]
Silver-β-alumina	Ag3*d*5/2	368.4	369.7	62–67
	Na2*s*	63.9	66.0	54–67
Lithium-β-alumina	Li1*s*	[a]	52.4	[a]
	Na2*s*	64.5	66.5	53–57
	Ag3*d*5/2	368.6	369.7	60–72

[a] Other peaks present are thought to be due to surface decomposition (*9*).

TABLE IV

SELF-POTENTIALS FOR SILVER ION SITES IN SILVER IODIDE AND SILVER MERCURIIODIDE

	Compound	Distribution of cations[a]	Self potentials (eV)			Charge at sites		
	Silver iodide	Low temperature form		−8.4			+1.0	
	Silver iodide	High temperature form	2*c*	3*c*	4*c*	2*c*	3*c*	4*c*
(a)		Two Ag$^+$ over all 30 sites	+2.5	+1.5	+1.8	0.0677	0.0677	0.0677
(b)		Two Ag$^+$ over six 2*c* sites	−4.3	+0.35	−1.7	0.3333	0	0
(c)		Two Ag$^+$ over twelve 3*c* sites	+2.4	−0.59	+3.0	0	0.1667	0
(d)		Two Ag$^+$ over twelve 4*c* sites	+5.3	+3.1	0.0	0	0	0.1667
(e)		One Ag$^+$ in 2*c* site, remaining structure totally averaged	−7.4	—	—	1.0	—	—
		One Ag$^+$ in 3*c* site remaining structure totally averaged	—	−7.6	—	—	1.0	—
		One Ag$^+$ in 4*c* site, remaining structure totally averaged	—	—	−7.4	—	—	1.0
	Silver mercuriiodide	Low temperature form	Ag(1)[b]		Ag(2)[b]	Ag(1)		Ag(2)
			−8.3		−8.5	+1.0		+1.0
		High temperature form: 2Ag$^+$ and one Hg^{2+} averaged over four sites		−8.5			+1.0	

[a] Crystal structures from Ref. (*13*).

[b] Designations as given in (*13*).

TABLE V

	Occupancy of sites		Self-Potentials (eV)	
Compound	BR	aBR	Br	aBR
Na-β-alumina	1	0	−12.7	− 6.2
	0	1	− 5.9	−13.1
	0.5	0.5	−11.7	−12.0
Ag-β-alumina	1	0	−14.95	− 7.8
	0	1	− 8.1	−14.7
	2/3	1/3	−14.2	−13.2

In this paper we will use self-potentials rather than Madelung constants, since in compounds where there are different ionic sites the self-potential is the value that must be taken in order to calculate a binding energy for an ion in a particular site.

Self-potentials for both forms of silver mercuriiodide and silver iodide have been evaluated using a program written by Picken and Van Gool (*11*). The calculations for the high temperature form of silver iodide were carried out with a variety of cation charge distributions (Table IV). In Table IV (a) is with the two positive charges totally averaged over all possible sites; (b), (c), and (d) are, respectively, with the two ions totally averaged over just the 2, 3, and 4 coordinate sites. None of these give a reasonable spread of self-potentials because in all cases one or more of the sites appear with a positive self-potential; such a value is unreasonable for a positive ion site, and furthermore, all the values are appreciably different from the value for the low temperature form (−8.4 eV). If, however, one silver ion (unit charge) is put in either a 2, 3, or 4 coordinate position in one unit cell and the remaining unit charge in that unit cell is spread out over the other possible sites and all the surrounding unit cells are averaged as in (a) the self-potentials for the three possible sites become negative, with nearly equal values, which are close to that for the low temperature form of silver iodide with a unit charge on the cation. Crystallographically, this arrangement of ions is equivalent to silver ions of unit charge being randomly distributed over the 2, 3, and 4 coordinated sites.

Calculations of self-potentials for sodium-β-alumina have already been carried out (*11*). We have extended these for an equal distribution of sodium ions between the two possible sites (Beevers Ross (BR) and anti-Beevers Ross (aBR)) to see if this results in a different

TABLE VI

COMPARISON OF LATTICE SITE SELF-POTENTIALS OF SODIUM AND SILVER β-ALUMINAS

Atom	Site	Equivalent in Na-β-alumina	Self-Potential Ag-β-alumina (eV)	Self-Potential Na-β-alumina (*11*) (eV)
Na/Ag	BR	BR	−14.95	−12.74
Al	Al(1)	Al(3)	−24.31	−39.43
Al	Al(2)	Al(2)	−31.82	−36.49
Al	Al(3)	Al(4)	−40.10	−39.43
Al	Al(4)	Al(1)	−35.78	−30.77
O	O(1)	O(1)	30.48	29.06
O	O(2)	O(4)	25.62	25.86
O	O(3) (4f)	O(2)	30.40	29.51
O	O(3) (4e)	O(3)	25.06	25.70
O	O(5)	O(5)	21.27	24.51

Note: These are calculated assuming a totally ionic lattice, i.e., with a charge of 3+ on the aluminium ions 2− on the oxygen ions and 1+ on the mobile cation.

TABLE VII
(A)

Compound	Self-Potential (eV)	K	$\lambda_c + \phi/R$ = shift/q	q (1)	q (2)	q (3)	Predicted shift			Experimental shift
							(1)	(2)	(3)	
Silver fluoride	−10.2	−2.9	−0.8	0.68	0.61	0.38	−0.5	−0.5	−0.3	+0.1
Silver chloride	−9.1	−3.4	−0.05	0.28	0.32	0.30	0.0	0.0	0.0	−0.2
Silver bromide	−8.7	−3.5	0.15	0.19	0.26	0.25	0.0	0.0	0.0	−0.3
Silver iodide (Low temperature form)	−8.4	−3.6	0.35	0.06	0.15	0.17	0.0	0.0	+0.1	+0.3
Cuprous chloride	−10.1	−3.8[b]	−1.8	0.28	0.32	0.30	−0.5	−0.6	−0.5	+0.6[c]
Cuprous bromide	−9.6	−3.7[b]	−1.2	0.19	0.26	0.25	−0.2	−0.3	−0.3	+0.6[c]
Cuprous iodide	−9.0	−3.8[b]	−0.7	0.06	0.15	0.17	0.0	−0.1	−0.1	+0.6[c]

TABLE VII
(B)

Compound	Self-Potential (eV)	K	$\lambda_c + \phi/R$ = shift/q	Experimental shift	q
Silver oxide	−11.5	−3.35	−2.5	+0.1	[a]
Silver sulphate	−9.89	−3.35	−0.9	−0.3	0.3
Silver orthophosphate	−9.5	−3.35	−0.5	−0.4	0.8
Silver perchlorate	−7.3	−3.35	+1.7	+0.2	0.1
Silver iodide[d] 2c	−7.4	−3.35	+1.6	+0.2	0.1
3c	−7.6	−3.35	+1.4	+0.2	0.1
4c	−7.6	−3.35	+1.4	+0.2	0.1
Silver mercuriiodide[e]					
Ag(1)	−8.3	−3.35	+0.7	+0.3	0.4
Ag(2)	−8.5	−3.35	+0.5	+0.3	0.6

[a] Recent work (*18*) gives a shift of −0.4 eV for silver oxide; this would suggest a partial ionic charge of ~0.2.

[b] Only the polarization energy correction.

[c] Adjusted literature values to the energy scale $\text{Au}4f_{7/2} = 84.0$ eV

[d] High temperature form.

[e] Low temperature form.

(1) On the basis of Pauling's electronegativities (*15*).

(2) $q = 0.129$ (difference in electronegativities of the anion and cation) (*16*).

(3) Using the method of equalization of electronegativities (*17*).

self-potential for the two sites. Also we have carried out similar calculations for silver-β-alumina (Table V). Table VI compares all the lattice self-potentials for silver-β-alumina with those of Ref. (*11*) for sodium-β-alumina.

As shown in Ref. (*9*), the term q_c/r in Eq. (1) may be replaced by $\lambda_c q_c$ where $\lambda_c = (\delta B_c/\delta q_c)$, λ_c is calculated as in Ref. (*9*) and values of 12.35 eV for silver and 12.1 eV for copper are obtained for $(\lambda_c + K)$, where K is a correction term. The term $(\lambda_c + K)$ compares the binding energy of an electron from a single ion in the gas phase to the binding energy of an electron from an atom in the metal; the value of

$(\lambda_c + K)$ is constant for all compounds of the same cation in the same oxidation state.

To obtain λ_c, the gas phase value must be adjusted for an ion in the particular lattice by a polarization and repulsive energy (*12*) for that lattice, which may be combined into the correction term K. We have calculated K for the silver halides and if we assume a partial ionic charge we are able to predict the experimental shifts. Three methods of calculating this charge are compared (Table VIIA).

In the case of the cuprous halides, lack of suitable data precludes the calculation of the correction for the repulsive energy. The sum of the two correction terms (K) has been found to be reasonably constant (*11*, *9*) for a series of compounds of the same cation. An average value of K, along with the observed experimental shift has been used to predict the partial ionic charge for the compounds in Table VIIB. In view of the extremely small shifts and the likely error in them (±0.2 eV) the calculated charges must be treated with extreme caution.

Discussion

a. Silver (I) and Copper (I) Compounds

These solid electrolytes showed very small shifts in binding energy; comparison with silver (I) and copper (I) compounds indicates this is general to all compounds of these elements in their univalent state (*6*, *19*). The calculated shifts (Table VII) show immediately that the range of shifts for these compounds will be very small; this is in contrast to the marked shifts observed in the compounds of some other elements. In view of the small size of the shifts in this case it is impossible to calculate the partial ionic charge accurately (Table VIIB). The results do show, however, that there is likely to be an appreciable amount of covalent character, even in these highly conducting solids (see also Ref. (*4*)).

The calculations of self-potentials for silver iodide (Table IV) show that the three sites are very similar if the more realistic model (e) is chosen. The self-potential of the high and low temperature forms are then −7.4 and −8.4 eV, respectively, assuming unit charge. For silver mercuriiodide there is very little change of self-potential for the high and low temperature forms.

It has been suggested (*4*) that the relative indifference of the silver and cuprous ions to their sites is one reason for the high conductivity of these compounds; the lack of shift would certainly not disagree with this.

b. The β-Aluminas

Sodium-β-alumina showed an additional peak at 66.8 eV with some samples but this was considered to be due to hydration by comparison with a hydrated sample. The calculations show the self-potentials of the BR and aBR positions to be very similar when individually occupied or when 50% of both are occupied (Table V). The existence of a single sodium peak in the spectrum would therefore be consistent with any of these arrangements if the degree of covalency in the two sites was also very similar. The X-ray crystallographic data suggest that the mid-oxygen positions are partially occupied rather than the aBR positions (*20*). It is difficult, however, to calculate the self-potential corresponding to this configuration. The residual sodium in silver and lithium-β-alumina showed a considerably broader peak which was deconvoluted (Table III). This could be due to the sodium ions being trapped at intermediate sites in the lattice. The binding energy of the sodium 2*s* electron in sodium-β″-alumina is very similar to that of the sodium in β-alumina. In both sodium-β-alumina and sodium-β″-alumina the majority of the sodium ions are in the BR position (*22*).

The silver ions in silver-β-alumina are thought to occupy the BR and aBR positions. The calculations show the self-potentials of the BR and aBR positions to be very similar when individually occupied (Table V). A difference of 1 eV in self-potential can be obtained by spreading the ions out with 2/3 in the BR positions and 1/3 in the aBR positions to give a 2:1 ratio BR:aBR. Such a spreading out would take place by thermal motion which has a time scale of the order 10^{-12} sec, and it is unreasonable to use the self-potential obtained from the spread out distribution for calculating binding energies for the photoelectron process which has a time scale of the order 10^{-16} sec. In other words a core electron in silver is

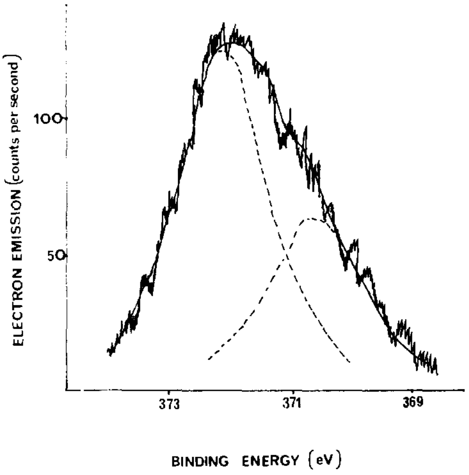

FIG. 1. The silver $3d5/2$ electron peak for silver-β-alumina. The dotted lines suggest how the peak may be deconvoluted with the peak areas in the ratio 2:1. The peak widths at half height have been taken as 1.7 eV for the best fit. This compares with 1.6 eV for the same peak for silver oxide. The binding energy scale is as measured and is, therefore, not corrected for sample charging or the spectrometer work function.

always associated with one silver nucleus and not 1/3 or 2/3 of a silver nucleus. The BR and aBR position may thus be taken to have the same self-potential, and if this is the case, Eq. (1) shows that the binding energy of a silver ion in the BR position will only be different from that of a silver ion in the aBR position if there is a difference in the charge on the silver ion (q_c). The ESCA spectrum (Fig. 1) gives two peaks at 369.7 and 368.4 eV in the intensith ratio 2:1, thus the peak at 368.4 eV must correspond to a smaller q_c on the silver ion, and the peak at 369.7 eV to a large q_c on the silver ion. On the basis of a 2:1 ratio BR:aBR, the peak at 369.7 eV would correspond to the silver ion in the BR position, and the peak at 368.4 eV the silver ion in the aBR position, and the aBR position would correspond to the most covalent silver ion site (smaller q_c). This agrees with the X-ray crystallographic results, which show that the smallest silver–oxygen distance in the aBR position is 2.424 Å, whereas in the BR position it is 2.809 Å, implying considerably greater covalent bonding in the aBR position. The results also agree with infrared studies of the external vibrations of the silver ion (*21*).

The possibility of X-ray reduction and compound decomposition cannot be entirely ruled out, but we have not observed any signs of it for silver compounds other than the iodate. If for example, silver nitrate is run at very low X-ray flux no additional peaks are observed. In the case of lithium-β-alumina, however, additional peaks observed at 50.5 eV and 49.0 eV binding energy may correspond to lithium oxide and lithium metal, respectively, consistent with previous studies that suggest that this is due to surface decomposition, as all lithium compounds we have studied decompose to varying extents (*9*).

Acknowledgments

We would like to thank Professor Van Gool for giving us his program for the calculation of Madelung potentials. One of us (A. F. P.) would like to thank the S.R.C. for a maintenance grant. We also thank P. M. Willis for the sample of silver rubidium iodide, Dr. R. A. Wiggins for samples of silver- and lithium-β-aluminas and Dr. M. J. Hopkinson for the sample of silver selenide and Mr. J. Sudworth for the sample of sodium-β''-alumina.

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