composition of alkyl halides is chlorine atom abstraction by the excited mercury atom.

$$RCl + Hg^* \longrightarrow R + HgCl$$

In the triplet cadmium photosensitized decomposition of paraffins the major primary step is C–H bond cleavage which becomes energetically feasible only if the process is a true hydrogen transfer.

$$RH + Cd^* \longrightarrow R + CdH$$

The formation of CdH in the course of the reaction can be readily detected spectroscopically.[20,21] Finally, hydrogen abstraction by excited triplet reagents such as $^3(n,\pi^*)$ benzophenone, acetone, etc., are well known in organic photochemistry.

In considering the general facets of excited-state chemistry, one notes the enhanced stability of the reaction complex arising from the higher polarizability of the excited atom. Also, the presence of the larger number of available reaction channels renders the excited chemistry more complex than that of ground-state systems and causes a pronounced departure from simple second-order kinetics on the microscopic scale.

Decomposition of the paraffin occurs *via* a predissociative step, and interconversion of Hg* and Hg^0 atoms *via* internal conversion of the reaction complex in competition with radiative decay from the (RH·Hg)* surface. Internal conversion, resulting in spin-orbit relaxation, requires a considerably higher molecular compression and shorter RH···Hg* bond distance than predissociation, leading to cleavage of the R–HHg bond. This indicates that in the reaction complex the total angular momentum vector remains well defined and consequently the reaction model, as outlined here incorporating only two reaction surfaces, is probably an oversimplified representation of the reaction system. Moreover, the *A* factors of the overall quenching reactions are high and therefore symmetry restrictions on the internal process cannot be severe. If this is the case then the noncrossing rule,[22] that two states belonging to the same irreducible representation always avoid crossing, would also require a different surface for each internal process.

The observed pressure dependence of the molecular band fluorescence maxima would seem to suggest that at high pressure vibrational relaxation of the reaction complex may be occurring. This, however, should alter the relative yields of the various primary steps, for which no experimental evidence exists at present.

Further experimental and theoretical studies are currently in progress and will be reported at a later date.

Acknowledgments. The authors thank the National Research Council of Canada for financial support and Dr. E. M. Lown for reading the manuscript.

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Inner-Orbital Photoelectron Spectroscopy of the Alkali Metal Halides, Perchlorates, Phosphates, and Pyrophosphates

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Abstract: Binding energies for Li "1s," Na "1s," K "$2p_{3/2}$," Rb "3d," Cs "$3d_{5/2}$," F "1s," Cl "2p," Br "3d," I "$3d_{5/2}$," O "1s," and P "2p" orbitals, when appropriate, were measured on crystalline alkali metal halides, perchlorates, phosphates, and pyrophosphates. The range of the observed binding energies was found to be narrow (within 2 eV) for each of the alkali metals in the various salts studied, whereas a somewhat greater range (*ca.* 3 eV) was found for the halogens in the alkali metal halides. The range of phosphorus binding energies in the phosphates and pyrophosphates was also small (*ca.* 1 eV and 2 eV, respectively). The variations in the experimental binding energies of the alkali metal halide salts were found to parallel the variations in the respective orbital energies calculated for the corresponding gaseous diatomic molecules in a near-limit Hartree–Fock approximation.

Since the main thrust in the study of solid materials by inner-orbital photoelectron spectroscopy (ESCA)[2,3] has been on covalently bonded molecules, it seemed desirable to extend this technique to a systematically selected array of anhydrous crystalline salts. Traditionally, the alkali metal halides have been considered as typical ionic lattice structures, so we have focused on these compounds. The perchlorates and orthophosphates were included since they represent the common MO_4 type of anion. In addition, the pyrophosphates were run in comparison with the orthophosphates.

Experimental Section

The inner-electron binding energies reported herein were obtained from a Varian induced-electron-emission (IEE) spectrometer[4] which

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is of the electrostatic electron analyzer type, with μ-metal shielding from external magnetic fields. The electrons were photoejected by Al Kα X-radiation (1486.6 eV) and subsequently retarded to an analyzer energy of 100 eV. The high level of reproducibility and instrumental resolution obtained from the Varian spectrometer has been demonstrated in previous work.[5] The relative atomic sensitivities of detection for the Varian spectrometer have recently been investigated.[6] The present measurements were corrected for possible charging effects by assigning a value[7] of 285.0 eV to the C "1s" reference line resulting from the thin layer of residual hydrocarbon,[8] perhaps coming from volatilization of traces of the Scotch-tape adhesive.

The alkali metal halides and perchlorates were commercially available samples of high purity. Several of the phosphates and pyrophosphates were similarly purchased although a few were prepared according to standard procedures. The alkali metal halides were dried in an oven at *ca.* 125° for several days and then placed along with all of the other samples into a vacuum dessicator and dried over P_2O_5 for a period of 1 week. The samples were subsequently removed and sealed in a drybox. For most of the samples an acceptable procedure was to transfer rapidly the material from the sample vial to the sample probe which was immediately placed in the outer vacuum lock of the spectrometer and evacuated. Each sample was degassed for a short period of time before being introduced into the high-vacuum area of the spectrometer (*ca.* 1×10^{-6} Torr). However, it was found necessary to heat some of the more hygroscopic samples to a high temperature in an evaporating dish just prior to placing them into the spectrometer in order to obtain reproducible binding energy values. Except for KCl, which exhibited a faint blue color when removed from the spectrometer, there was no evidence for the production of "color centers" by the X-radiation. For the KCl there was no change in the positions of the K "$2p_{3/2}$" and Cl "2p" spectral lines during the formation of the blue coloration.

Results

The measured binding energy data for the alkali metal halides are reported in Table I along with some corresponding theoretical values estimated (see Discussion) from orbital energies[9] of the diatomic alkali metal halide molecules. The binding energy levels measured for the alkali metals were Li "1s," Na "1s," K "$2p_{3/2}$," Rb "3d," and Cs "$3d_{5/2}$," while those of the corresponding halides were F "1s," Cl "2p," Br "3d," and I "$3d_{5/2}$." These energy levels were generally the ones giving the most intense spectral line.[6] Unfortunately the Li "1s" line in LiI could not be clearly observed because of the appearance of an intense peak which was probably the iodine "4d" spectral line.

Table I. Measured and Estimated Binding Energies (eV) for the Alkali Metal Halides (MX)

		F "1s"	Cl "2p"	Br "3d"	I "$3d_{5/2}$"
Li "1s"	M	55.9[a]	56.3	57.0	
		(53.8)[b]	(54.8)	(54.7)	
	X	685.2	198.7	69.4	619.1
		(684.9)	(199.2)	(70.5)	
Na "1s"	M	1071.0	1071.4	1071.6	1071.6
		(1071.1)	(1072.0)	(1071.9)	
	X	683.9	198.4	68.9	618.9
		(683.7)	(198.5)	(70.0)	
K "$2p_{3/2}$"	M	293.3	293.0	293.1	293.0
		(294.1)	(294.9)		
	X	684.0	198.3	69.1	619.0
		(682.9)	(197.9)		
Rb "3d"	M	110.0	110.1	110.2	110.6
		(113.1)			
	X	683.8	198.1	68.6	618.4
		(682.7)			
Cs "$3d_{5/2}$"	M	724.2	723.9	724.2	724.1
	X	682.6	196.5	68.3	618.4

[a] Values referenced to "residual hydrocarbon," with C "1s" = 285.0 eV. [b] The values in parentheses are binding energies estimated by eq 1 from the orbital energies for the diatomic molecules.[9]

Table II shows the measured binding energies of the alkali metal perchlorates and potassium chlorate. The same alkali metal levels were measured along with the chlorine "2p" and oxygen "1s" levels. The measured binding energies[10] of the alkali metal phosphates and pyrophosphates are given in Table III. Once again, the same alkali metal levels are reported with the phosphorus "2p" and oxygen "1s" binding energies. The high reproducibility of the Varian spectrometer[5,11] eliminated the necessity for more than duplicate measurements on all of the samples; however, a standard

Table II. Measured Binding Energies of the Alkali Metal Perchlorates

				Shift of Cl "2p" from	
Compound	M[a,b]	O "1s"[b]	Cl "2p"[b]	MCl[b]	MCl[c]
$LiClO_4$	57.4	533.6	209.2	10.5	9.4
$NaClO_4$	1072.0	533.2	208.7	10.3	9.7
$KClO_4$	293.6	532.4	209.0	10.7	10.1
$KClO_3$	293.4	532.5	206.7	8.4	8.0
Mixture of					
$KClO_4$			208.3	8.8	
$KClO_3$	293.9	532.7	206.3	6.8	
KCl			199.5	0.0	
$RbClO_4$	110.6	533.0	208.6	10.5	10.0
$CsClO_4$	724.4	532.9	208.4	11.9	11.4

[a] The measured binding energies of the alkali metals refer to the orbitals indicated in Table I. [b] Values referenced to residual hydrocarbon, with C "1s" = 285.0. [c] Assuming a constant binding energy for the alkali metal M in MCl, $MClO_3$, and $MClO_4$.

Table III. Measured Binding Energies[a] of the Alkali Metal Phosphates and Pyrophosphates

Compound	M[b]	P "2p"	O "1s"
Li_3PO_4	55.6	133.8	531.7
$Li_4P_2O_7$	55.8	134.5	531.9
Na_3PO_4	1071.1	132.7	530.7
$Na_4P_2O_7$	1071.0	133.3	530.8
K_3PO_4	292.7	133.4	530.6
$K_4P_2O_7$	292.4	132.8	530.3
Rb_3PO_4	110.2	132.7	530.5
$Rb_4P_2O_7$	110.2	133.3	530.9
Cs_3PO_4	724.1	132.3	530.3
$Cs_4P_2O_7$	724.0	132.8	530.4

[a] Values referenced to "residual hydrocarbon," with C "1s" = 285.0 eV. [b] The measured binding energies of the alkali metals refer to the orbitals indicated in Table I.

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(11) We are happy to note that binding-energy values reported for LiF, NaF, RbF, NaCl, NaBr, and NaI, as measured on another Varian instrument similar to ours without correcting for surface charging by use of a reference standard, were very close to our similarly uncorrected measurements; see ref 19.

deviation of *ca.* ±0.2 eV was found for the compounds on which more replicates were run. The absolute values of the binding energies may be known with somewhat less certainty because of the inherent difficulties of measuring solids (particularly semiconducting and insulating samples) due to uncertainties in the reference levels and surface-charging effects.

The desirability, for intercomparison purposes, of measuring all of the values reported in Tables I through III on the same spectrometer using the same referencing technique is demonstrated by the comparison of our work on alkali metal salts with some miscellaneous values[2,12–19] reported in the literature for these compounds. Thus, values of 686.3 and 685.4 eV have been reported[17] for the F "1s" binding energy in lithium and sodium fluorides, respectively. Note that these values are 1.1 and 1.5 eV higher than the ones given in Table I. Part of this difference (0.5 eV) is accounted for by the fact that we measure the binding energy of their reference standard Au "$4f_{7/2}$" to be 83.5 eV; whereas 84.0 eV was chosen in the other study. It should also be noted that a value of 686.1 eV was reported[15] for the F "1s" in LiF by a group who have also reported[15] the C "1s" line of graphite to be at 284.3 instead of at our value of 283.9 eV. Further, the literature value[14] for sodium chloride agreed with our data as to the Cl "2p" binding energy but was 1.3 eV higher than our value for the Na "1s." The Br "3d" binding energy in KBr has been reported[16] as being 0.9 eV higher than our value. Unfortunately, the information given in these latter studies was insufficient to decide how much of the observed differences could be attributed to the referencing.

Some of the problems inherent in changing the method of referencing are illustrated by the data in the last two columns of Table II, which show the shift in the chlorine "2p" binding energies of potassium chlorate and some perchlorates as reported from the respective alkali metal chloride. Note that, when the primary referencing is to the carbon "1s" binding energy of the residual hydrocarbon, a different value is obtained than when a constant binding energy is assumed for the alkali metal in its salts with the chloride and the oxychloride anions. This latter form of referencing has previously been utilized[12,16] in reporting data; and the literature value[12] for the NaCl–$NaClO_4$ difference of 9.5 eV according to this procedure is in good agreement with the value of 9.7 eV given in Table II. As shown in this table, when the difference in Cl "2p" binding energy between either $KClO_4$ or $KClO_3$ and KCl was measured directly in a mixture of these salts, the values are *ca.* 2 eV lower than when the binding energies were measured on each of these three salts separately with referencing to the "residual hydrocarbon." We have previously reported[5] that the surface charging of one particulate solid appears to be affected by neighboring solid particles. Although several authors have noted[2,12,16] that the salts of alkali metal cations with halogen and oxyhalide anions exhibit essentially constant binding energy, this has been contradicted by binding energy measurements[13] on a variety of potassium salts. The K "1s" binding energy for KI was found to lie 1.3 eV above the values observed for KIO_3 and KIO_4, and the K "3p" binding energies of the potassium halide salts were found to exhibit significant variations in their valence binding energy values. In the data reported in Tables I–III, we find the following approximate ranges of binding energies for the alkali metals: Li "1s," 1.8; Na "1s," 1.0; K "$2p_{3/2}$," 1.2; Rb and Cs "3d," 0.6 eV.

Discussion

The main thrust thus far in inner-orbital photoelectron spectroscopy of solids[2] has been in the study of atoms in molecules (including a few molecule ions), and most investigators have found it convenient to interpret their results in terms of charge transfer within a molecule without taking into account solid-state effects attributable to the packing of the molecules into a close three-dimensional array. The validity of this approach is demonstrated by the fact that measurements of a given binding energy in a series of carbon compounds[7] show nearly the same differences (chemical shifts) when the studies are done in the gas or solid phase, even though the absolute value of the binding energies for the gaseous measurements are considerably higher than those of the solid measurements because of the basic difference in reference energy levels.[20] In view of the success of this approach, we are extending it to the treatment of the alkali-metal halides, which are usually viewed[13,17,18] in terms of the ionic-lattice model.

To a good approximation, it has been found[5,13] that the "chemical shift" in binding energy (experimental) or in orbital energy (theoretical) from one compound to another is essentially the same for all of the inner orbitals of a given atom. We have checked this matter of the constancy of the chemical shift for the alkali metal halides by comparing the changes in orbital energies for all of the inner orbitals of potassium and of rubidium in going from the neutral atom to the diatomic alkali metal fluoride molecule to the isolated cation and have found that the chemical shifts in orbital energy are about the same for all of the inner orbitals. Similar results were found for bromine and chlorine. Therefore, absolute values of the orbital energies calculated for the same orbitals for which binding energies were reported in Table I are intercompared in Figure 1, using values taken from near-limit Hartree–Fock SCF computations.[9,21–23]

As expected from the atomic-charge concept,[2] going from the neutral atom to the singly charged anion in

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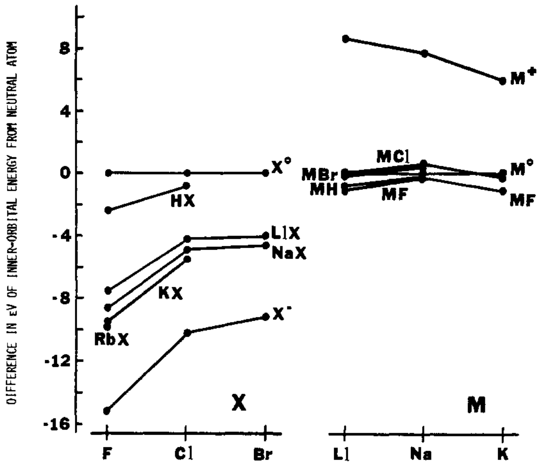

Figure 1. Comparison of selected inner-shell orbital energies (F "1s," Cl "2p," Br "3d," Li "1s," Na "1s," and K "2p") calculated with near-limit Hartree–Fock STO bases for the diatomic molecular alkali metal halides (MX), the respective neutral atoms (M^0 and X^0), their ions (M^+ and X^-), and hydrides (MH and HX).

Figure 1 for the halogens gives a reduction in the absolute value of the inner-orbital energy; whereas, going from the neutral atom to the cation for the alkali metals leads to an opposite change. Not surprisingly, the inner-orbital energies given in Figure 1 for fluorine and chlorine in their hydrogen halides[9] are shifted only a small distance toward those of the anion from the values corresponding to the neutral atom, while a considerably greater shift (but only a little more than half way) is found for the halogens in the diatomic alkali metal halides.[9] The fact that the orbital energies for the alkali metals in their diatomic halides exhibit inner-shell orbital energies close to those of the neutral atom (Figure 1) is difficult to explain on a simple charge-transfer basis.

In trying to compare experimental inner-orbital binding energies (b.e.) with the calculated orbital energies (ϵ) of related molecules, using Koopmans' theorem,[24,25] it was noted that the binding energies measured on solids were nearly linearly related to the respective orbital energies, with the difference increasing slightly with increasing energy, and that a single equation seemed to account for all of the comparable data on molecules and a few atoms. A difference plot to show this effect is given in Figure 2, which includes some data on systems other than the alkali metal halides.[9,21,26,27] The equation for the curve presented in this figure is given in eq 1.

$$\Delta = -\epsilon - \text{b.e.} = 10.8 - (2.6797 \times 10^{-2})\epsilon - (8.5293 \times 10^{-6})\epsilon^2 \quad (1)$$

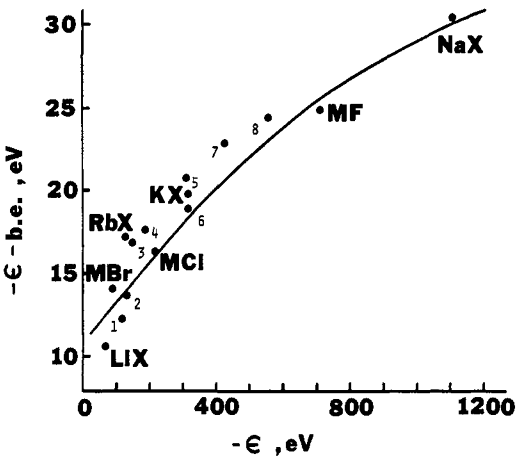

Figure 2. Differences between orbital energies (ϵ) and binding energies measured on solids *vs.* the orbital energies (ϵ) calculated for the respective isolated molecules or atoms. The binding energies in eV were determined for various solids, including the crystalline alkali metal halides (MX), from which the line in this plot was obtained by a least-squares treatment (see eq 1) of the appropriate data. The absolute values of the corresponding orbital energies ($-\epsilon$) were taken from near-limit Hartree–Fock calculations of the respective simple molecules or atoms. The numbers stand for the following species: 1, SiO (Si "2p"); 2, BeO (Be "1s"); 3, P (P "2p"); 4, S (S "2p"); 5, H_2CO (C "1s"); 6, CO_2 (C "1s"); 7, NH_3 (N "1s"); 8, BeO (O "1s").

Using this equation, the values of the binding energies for the diatomic alkali metal halides shown in parentheses in Table I were estimated from the corresponding near-limit Hartree–Fock orbital energies calculated for these molecules.[9] Note the good agreement between the values thus obtained for the (gaseous) diatomic molecules and those measured for the corresponding salt crystals. In both cases, an appreciable spread in inner-orbital binding energy is to be seen for the halogens with little for the alkali metals.

Interpretation of Mulliken electronic populations,[28] as well as the orbital-density distributions and the forces exerted on the nuclei,[29,30] show that the two σ-type valence orbitals in the diatomic LiF molecule correspond to electrons associated almost completely with the fluorine atom; whereas, the two π-type orbitals (the outermost ones) correspond to a sharing of the charge density, as in a rather weak triple bond between the lithium and the fluorine. Table IV shows that this idea may be extended to the diatomic alkali metal halides other than lithium fluoride, since the difference in orbital energy[9] between the outermost π orbital of an alkali metal diatomic molecule of a given halide and the outermost p orbital[21] of the respective halogen atom is found to be nearly the same size and to vary in the same way from one alkali metal to another as the difference from atom[21] to molecule[9] calculated for an inner orbital of the respective halide.

One might envisage similar bonding in the alkali metal halide crystals, with the valence p orbitals of the constituent halogen atoms contributing approximately two-thirds of their p character to π-type orbitals and one-third to σ-type orbitals—with covalent bonding to the metal atoms occurring *via* the π-type orbitals.

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(27) The corresponding measured binding energies of the species shown in Figure 2, excluding the alkali metal halides, are given in the following: SiO, R. Nordberg, H. Brecht, R. G. Albridge, A. Fahlman, and J. R. Van Wazer, *Inorg. Chem.*, 9, 2469 (1970); BeO, see ref 15; P, see ref 10; S, B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling, and K. Siegbahn, *Phys. Scr.*, 1, 286 (1970); H_2CO and CO_2, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 9, 612 (1970); NH_3, D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *ibid.*, 8, 2642 (1969).

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Table IV. Decreases in Selected Orbital Energies When Going from the Halogen Atoms to Their Diatomic Molecules with Alkali Metals

	$-\Delta\epsilon$, eV	
Diatomic molecule	Outermost π orbital[a]	Inner orbital[b]
LiF	7.1	7.5
NaF	8.3	8.7
KF	9.0	9.5
RbF	9.1	9.7
LiCl	3.6	4.2
NaCl	4.3	4.9
KCl	4.9	5.6
LiBr	3.2	4.1
NaBr	3.9	4.6

[a] Orbital-energy differences corresponding to differences in the first-ionization potentials. [b] Differences for the "1s" orbital of fluorine, "2p" of chlorine, and "3d" of bromine.

Some experimental support for this idea is obtained by comparing first-ionization potentials as measured on the diatomic gaseous alkali metal iodides[31] (for which such data are available) with the appropriate inner-orbital binding energies reported in Table I for the respective alkali metal iodide crystals. Remembering that the experimental error in the ionization potentials as well as in the inner-orbital binding energies is around ±0.2–0.3 eV, we see that the following comparison of differences from the values for lithium iodide in first-ionization potentials and in inner-orbital binding energies (in parentheses) is about what would be expected from an extrapolation of the values of Table IV to the iodides: NaI, −0.1 eV (+0.2 eV); KI, +0.4 (−0.1); RbI, +0.6 (+0.7); and CsI, +0.7 (+0.7). It thus seems that the variations in inner-orbital binding energy of the alkali metal halides may very simply be accounted for by a molecular-binding approximation, with the ionic lattice being ignored.

The arguments in the preceding two paragraphs are borne out by the fact that the fluorine "1s" binding energy in the alkali metal fluorides is in the range of 683–685 eV; whereas a binding energy of 688 eV is found in two structures[32] in which fluorine is directly bonded to the phosphorus and even higher binding energies around 690–691 eV are observed[33] for fluorine atoms bonded to carbon. Increase in binding energy is interpreted[2] in terms of more sharing of the fluorine electrons with the other atoms. Similarly, the chlorine "2p" binding energy in transition metal complexes[34,35] is found to be slightly higher than the values reported here for the alkali metal chlorides.

It should be noted in Table II that the lithium and sodium binding energies of the perchlorate salts are larger than equivalent binding energies reported in Table I for any lithium or sodium halide, so that in this respect the perchlorate anion is equivalent to a halogen of high atomic number (say, astatine). In comparing the lithium and sodium binding energies reported in Tables I and III, the opposite is seen to be true for the phosphate and pyrophosphate. Unfortunately, the observed differences between metal binding energies in the salts of the heavier alkali metals (K, Rb, Cs) are probably too small to be simply interpretable. In view of the fact that the perchlorate is known as a noncomplexing ion,[36] while the ortho- and pyrophosphates form relatively strong complexes, even with the alkali metals,[37] we infer that the bonding (π type) between the metal and the halogen decreases when going from fluoride to iodide.

In the work reported here, we have interpreted experimental data on the binding energy differences between the alkali metal halides (as well as other substances based on these atoms) in terms of the effects of covalent bonding in their crystals; whereas Citrin and Thomas have based their interpretation[38] on the usual electrostatic ionic model. Thus, it appears that this type of experiment does not distinguish between the two extremes of the ionic and covalent explanations. We believe that many of the differences between various predominantly ionic solids might equally well be interpreted in terms of variations in covalent bonding as by the usually methodology of solid-state physics.

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