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CORRELATION OF MATERIALS PROPERTIES WITH THE ATOMIC DENSITY CONCEPT

Report No. 5

FOREWORD

The work reported herein was initiated in Contract NAS8-28517 under NASA Control No. PR- M- 28517, under technical monitors Daniel W. Gates (Principal) S&E-SSL-TT and Tommy C. Bannister (Alternate) S&E-SSL-TR, of NASA Marshall Space Flight Center to Nevada Engineering and Technology Corporation, Long Beach, Calif.

This report describes progress in developing, through mathematical expressions, values for the parameters which apparently determine the values of atomic density, melting point, and principal elastic constant for the alkali halides. This necessarily required the review and refinement of these data for the monohalides in general and for LiH. A more sensitive and dimensionless expression of the mass factor appears to have promise and a still more sensitive one is suggested for future study. A periodicity factor based on inert gas core configuration has been suggested to replace the atomic number previously used.

The method applied during this exploratory study involves the investigation of the derived value for the atomic density and for at least one other measured property for a given subgroup, first of elements, then of the equivalent compounds of an element. In this report are such relations for the alkali halides in which the atomic masses of metal and halide are most nearly equal.

The objective of this project has been, through constant striving for exact agreement with measured properties, to refine and broaden the atomic density concept and its application to the prediction of property values and the understanding of materials behavior. Wherever a novel expression or relation has been found, an attempt has been made to confirm or deny it by example. Nevertheless, the relatively small number of elements and compounds so far tested, and the possibility that some physical data are in error, suggests the precautionary advice that some of the relations may be fortuitous or in error.

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ABSTRACT

The discovery that a somewhat crude "mass factor" appears capable of eliminating the last few percent of error in relating the measured properties of atomic density, melting point, and another property of elemental metals according to their "natural" isotopic content has been reported. Since all compounds represent far larger differences in atomic mass, it was hoped that this factor might be suitable for studying a selected number of them. The group chosen comprises the monohalides.

The expressions obtained showed the factor mf to be too sluggish and to be dimensionally linked with the atomic weight. A simple dimensionless factor tested is $f = (W_X - W_M)/W$ which served to simplify the derived empirical expressions and showed that in these compounds, the mass-momentum effect is about twice as great for the compounds in which the metal is lighter than the halogen as for the compounds in which the situation is reversed.

Using the factor f, the compounds LiH, NaF, KCl, RbBr, and CsI were used to show that the atomic number Z does not serve well as the "yardstick" parameter, and the factor n, based upon the principal quantum number of the inert gas shell most nearly representing that of the mean of cation and anion has been tested. With either f or a still more sensitive factor in which W is replaced by the atomic mass of the lighter constituent, the calculated value for LiH is a credible one.

With the proposed work nearly completed, it is concluded that the atomic density is indeed a practical, accurate, and tractable characterizing parameter, without which it is improbable that the mass factor or the periodicity factor could so quickly be developed and tested.

Recommendations are made for work to be undertaken in the future. This includes, in addition to broadening and refining the atomic density and the property to which it may relate, a brief plan for a study to settle upon the proper expression for precomputing both factors.

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New Terms:

The "periodicity factor" with symbol n was so noted but not named in the First report. The values of n are certain only for Ar, Kr, and Xe as 2, 3, and 4 respectively. From earlier work n_{Ne} is estimated to be about 1.1+ and n_{He} between 0.17 and 0.2 . In the equipoise salt KCl the value of n is the same as n_{Ar}; it is the mean of the values applying to the inert gas which is the "core" of the ion which forms.

Reference

1. "Atomic Geometry of the Alkali Halides", AFML -TR-66-413

CORRELATION OF MATERIALS PROPERTIES WITH THE ATOMIC DENSITY CONCEPT

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INTRODUCTION

The atomic density of a substance is no more than a count of the number of atoms in a unit volume of it. For an element, $N = (\rho \cdot Av)/W$, where ρ is the real density, Av is Avogadro's number, and W is the atomic weight of that element. The atomic density is thus inversely linear to the familiar atomic volume often used in solid-state physics, but it has the advantage of being more tractable in such Law of Mixtures computations as may be needed for mixtures or compounds.

In a compound, the "atom" is fictional in that represents the chemical composition and hence all elements present; the atom of NaCl thus has a mass equal to half the molecular weight of NaCl. One sees that any substance can be characterized by a value of N provided its real density and chemical composition are known. In this work, the convenient unit for atomic density is 10^{22} atoms/cc, so that values of N customarily lie, in solids, from values slightly below 1 (for cesium) to 17.6 for diamond. Since N is derived from density values it is of course changed by changes in temperature and pressure; the values used thus far result from densities measured at (or corrected to) 298.1K and one atmosphere.

The existence of N atoms/cc reflects the existence of N bonds/cc among them, so mathematical expressions can be derived in which this "bond density" can be separated from the factors which determine bond "strength". An intriguing result of the work has been the discovery that N can itself be regarded as a characteristic property and related to such parameters at the atomic number Z and the atomic weight W; in the course of this development it was observed that these relations among metal subgroups were more accurate when the number and masses of their isotopes are taken into account as well. On the premise that additional energy can be absorbed by a crystal if two or more isotopes are present in it, the concept of the "mass factor" has been cursorily tested and shown to permit, both for melting points and for N values, expressions to be developed for those elemental subgroups having similar bonding (valence) electrons. The finding that boron reasonably obeys such an expression derived from Sc, Y, La, and Ac, and that graphite similarly accords with Ti, Zr, and Hf has been followed by empirical accordance of Na with Cu, Ag, and Au and of Mg with Zn, Cd, and Hg.

These modest modifications of the Periodic Table arise, of course, among real crystals of the same substance. When it was observed, however, that the elastic constants of the body-centered cubic transition metals can be correlated within ± one percent from their MP and N values it appeared to be possible that the effect of mass-momentum in lattice vibration was perhaps more influential than had been supposed. In the elemental crystal of K, for example, one presumes attraction through valence electron interaction or transfer, the atoms thus being brought together so closely that orbital overlap began to occur. But in comparison to Na and Rb, this force of repulsion seems unaccountably small, and the density of K is lower than that of Na. An odd and surely related fact with the alkali halides: the K salts are the least dense for any one halogen, the chlorides are least dense for any one metal, and KCl is lowest in density for the series. Since the ratio W/Z is lowest for K and Cl it appeared at least possible that to the early idea that K is larger than its mass would indicate, the obverse,- that the K atom appears large because it is light,- ought to be added. An intuitive mechanism might well be the simple observation that for a given energy content, a light atom must vibrate over a larger amplitude, and hence appear to be larger since overlap repulsion would be exerted on it by but a few neighbors at a time, than would a heavier one of the same electronic configuration, and brief assessment of this effect in a few light isotopes and for most elements disobeying the rule of Dulong and Petit. The studies reported earlier not only descried this mass-momentum effect on N, Θ_{298}, and MP but showed that it is negligible for monoisotopes, smaller for heavy metals than light ones, but effective enough to produce measurable change even when the element contains only a few percent of an isotope differing from the dominant one by 2 awu.

It appeared that since the whole of the mass effect $W^{y}\ mf^{yz}$ can be regarded as the "effective" mass, the two could somehow be precombined, with the following objectives:

With but three unknowns, three subgroup members can be used to derive them and the fourth used as a check on validity,

Specific questions regarding apparent exceptions can be answered by introduction of other candidate terms.

At the same time, the method employed can be illustrated for future computer studies in which the constrictions placed on the logarithms of a quantity which may in some cases be negative can be avoided.

In the first Report, preliminary data regarding the melting points and atomic densities of the alkali metal halides were used to show that those in which the atomic masses of the two components were most nearly equal (called the "equipoise compounds)[1] were clearly dominated by the N and MP values of the metals themselves. It was decided, therefore, to reexamine the sixteen I-A halides (all but three of which form the rock-salt structure) and study, as well, the fourteen I-B monohalides, most of which exhibit cubic or slightly deformed halite structures and one of which (AgI) forms the as-precipitated hexagonal structure, transforming irreversibly into a denser structure at an elevated temperature. (Note that this behavior is quite different from the lanthanons, the majority of which form bcc crystals only at elevated temperatures). It was hoped that data would be sufficient to develop and test a number of candidate versions for the factor mf.

THE MONOHALIDES: STUDY OF ATOMIC DENSITY AND MELTING POINT VALUES

A basic subsumption of this work has been that the temperature threshold of melting is (except where incongruent) an accurate and sensitive measure of the product of the bond strength and bond density in a solid. Since N is a measure of bond density (and can be related in a subgroup to Z, W, and mf) one can hope to develop a combined relation which will illuminate the influence of any single parameter upon bond strength.

Table 1 shows the pertinent data. Each column will be separately discussed.

The values of N have been reviewed and these data supersede those used in the earlier Report. LiF is by far the highest and RbI lowest for the I-A halides. Note that N for the bcc CsCl is almost identical with that of CsF. In every metal grouping, the decrease in N with increasing Z is most notable between fluoride and chloride when there is no change in structure.

The packing efficiencies of those monohalides for which interatomic distances are readily available suffice to show (a) that the majority of salts lie close to but slightly below the ideal PE (52.37%) for the simple cubic structure which is the result of presuming "atoms" which have radii which are the sums of the half-radii of metal and halogen. Outstandingly different are overpacked LiI and underpacked CsF; NaF is also slightly overpacked.

The R_N values, are inversely related to the cube root of N. Thus while CsF and CsCl are almost identical, the R_N values are quite different by reason of the difference in coordination number and packing efficiency. Since it has heretofore been assumed that this difference is the result of changes in bond strength it is also subsumed that those changes will best relate to material behavior if no correction for ideality is initially made.

The "atomic" number Z for these compounds is simply the average value; one observes simple repetitions among them. It has been noted that the use of Z as a simple counter in these empirical expressions is not reflective either of elements in the short series nor of post-lanthanide elements, because the principal changes in valence do not happen to occur at recurring values of Z except for the region 14 Z 58, and since Li, Na, and F lie outside this zone there will naturally appear to be unreconcilable differences between these elements (and their compounds) and the remainder.

To clarify this point (discussed briefly and inconclusively in earlier reports) let us take some number <u>n</u> which identifies in the simplest possible way the <u>periodicity</u> of recurrence of a nominal valence of one for the 1-A and 1-B metals. From $n = (Z-1)/18$ or $(Z-2)/18$ one obtains values for n_M of:

	Li	Na	K	Cu	Rb	Ag	Cs	Au	^{65}Au	
n_M	.111	.555	1.0	1.555	2.0	2.555	3.0	4.333	3.550	or
	.0555	.50	.9444	1.50	1.944	2.50	2.944	4.278	3.50	

The relations are arithmetically simple and can serve very well for relative purposes. Using the first formula, n_X for F, Cl, Br, and I are found to be 0.555, 1.0, 2.0, and 3.0 when (Z+1) is used, and the value for Z for each monohalide derives from: $18\ (n_M + n_X)/2$.

But the use of Z (or of the n values derived above) can be seen from the table to serve poorly the role of periodicity; the arithmetic or geometric change in Z with a given metal, least between fluoride and chloride, is reflected by the largest change in N and elastic modulus throughout, but where the MP values of the Li salts are 256K apart, those of the K salts are, for a similar change in Z separated only by 105K.

No attempt will be made here to develop a more representative yardstick than Z, but it is hoped that this simple analysis will provide a credible approach for doingthis in the future.

The values of W/Z, from which 2 has been subtracted so that they can be seen more clearly, reflect not only the increasing nucleon/proton ratios of the heavier elements but the pronounced minimum in this ratio occurring with K, Cl, and their compounds. As stated in the last report, the simple ratio W/Z cannot be safely used to characterize an element or its compounds in terms of observed properties because x and y are not numerically equal. The data are included here for the use of those who would nevertheless use

Table 1

Pertinent Data for the Monohalide Salts

	N	PE	R_N	Z	(W/Z)-2	W	mf	f	MP	E	n
LiF	12.236	51.78	1.004	6	0.1615	12.969	3.4727	0.92986'	1143	70.35	0.5
LiCl	5.875	51.97	1.286	10	.1196	21.196	5.3398	1.3452'	887	26.46	1.0
LiBr	4.804	52.14	1.375	19	.2855	43.424	8.5422	1.6804'	820	20.05	1.5
LiI	3.654	54.39	1.506	28	.3900	66.921	10.953	1.7926'	719	13.69	2.0
NaF	8.004	53.49	1.161	10	.0994	20.991	1.9978	.19015	1235	26.93	1.0
NaCl	4.462	52.06	1.410	14	.0872	29.221	3.5303	.42651'	1074	12.81	1.5
NaBr	3.760	52.15	1.493	23	.2369	51.449	7.5445	1.1063'	1028	10.17	2.0
NaI	2.946	52.03	1.619	32	.3421	74.950	10.194	1.3864'	924	7.37	2.5
KF	5.141	51.29	1.345	14	.0750	29.050	4.4837	.69203	1154	12.90	1.5
KCl	3.205	51.90	1.574	18	.0710	37.277	1.9102	.09789	1049	6.38	2.0
KBr	2.783	52.03	1.650	27	.2040	59.506	6.3880	.6858'	1003	5.16	2.5
KI	2.272	52.15	1.766	36	.3057	83.003	9.3700	1.0578'	996	3.79	3.0
RbF	4.335	51.94	1.423	23	.2710	52.234	8.1530	1.2726	1032	8.90	2.0
RbCl	2.749	50.33	1.657	27	.2394	60.461	7.072	.8273	988	4.51	2.5
RbBr	2.440	51.42	1.724	36	.2970	82.690	2.358	.06725	955	3.43	3.0
RbI	2.013	51.80	1.838	45	.3598	106.190	6.437	.39019'	915	2.70	3.5
CsF	2.843	41.41	1.638	32	.3735	75.952	10.673	1.4997	957		2.5
CsCl	2.841	67.11	1.788	36	.3384	84.179	9.8718	1.1577	919		3.0
CsBr	2.490	66.74	1.869	45	.3644	106.410	7.280	.49803	909		3.5
CsI	2.091	67.37	1.981	54	.4055	129.904	2.450	.04619	894		4.0
	at/cc	%	Å			awu	awu	*	°K	GPa	*
CuF				19	.1721	41.269	6.6739	1.0793	1181		
CuCl	5.0372			23	.1520	49.496	5.0372	.56746	704		
CuBr	4.1813			32	.1735	71.724	4.0459	.22822'	771		
CuI	3.5544			41	.3255	95.222	7.9600	.66543'	878		
AgF	5.5547			28	.2655	63.434	9.4272	1.4010	708		
AgCl	4.6725			32	.2394	71.661	8.5098	1.01055	728		
AgBr	4.1519			41	.2900	93.889	5.2880	.29781	705		
AgI(β)	3.0832			50	.3477	117.387	4.3630	.16215'	831		
AuF				44	.4541	107.983	13.340	1.64812			
AuCl	3.8348			48	.4210	116.210	12.709	1.3898	443 d.		
AuBr	3.4365			57	.4287	138.438	10.819	.84556	388 d.		
AuI	3.0681			66	.4536	161.935	8.370	.43266	394 d.		

* see text for meaning of f and n

CsCl, CsBr, and CsI display a body-centered cubic structure. Most of the remaining salts exhibit the halite structure which, by reason of the reduction of a half-molecule to an atom, becomes simple cubic.

As-precipitated AgI is hexagonal and less dense than the cubic -form; if it is used, its N value is 2.916 x 10^{22} atoms/cc.

Salts showing a marked value of f are those in which the metal atom is lighter than the halogen atom.

Underlined values will be discussed.

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The data in this table supersede those of p 16, Report No. 1

this factor or a variant of it. That it has been insufficiently applicable in accurate data analyses lies largely in the simple fact that Z, the atomic number, cannot serve as a yardstick among members of a subgroup even of elements, since such a yardstick implies that all (or a fixed proportion) of the electrons present take part in the bonding process.

The values of W, however, are usually trustworthy, although some of the lighter elements, particularly Li, may deviate appreciably from "accepted" values. For the compounds, the W values are obtained simply using the Law of Mixtures and assuming ideal stoichiometry.

The mf values, discussed in the previous report and satisfactory for polyisotopic elements, were tested here in a preliminary study of the mathematical expressions relating MP and N with Z, W, and mf. It was hoped that such expressions might be comparable.

In all cases the general expression in logarithmic terms is:

$$\text{Log } P = x \text{ Log } Z + y \text{ Log } W + yz \text{ Log mf} + \text{Log } C$$

, where P is the property E, MP, or N . The required four salts in each subgroup were obtained by regarding Na as a I-B element; in no instance was the Na salt consonant with values obtained from the Li, Rb, K, and Cs halides.

It is concomitant with the finding (that Na cannot in this way be included with the other alkali metals) to conclude that neither can F be thus included with the heavier halogens. Thus no subgroup of a given metal contains more than three salts. Accordingly, grouping was done for each halogen, with the assumption that the values for fluorides would not show a discernible trend when compared with chloride, bromide, and iodide groups. That this is clearly true can be seen from Table 2.

That the ratio $-x/(y+yz)$ should be slightly larger than unity and increase with the heavier halides is simply a reflection of the average W/Z values.

The values of mf contain the dimension of atomic mass and are therefore relatable to y through z, which may be thought of as relating to the effectiveness with which dissimilar masses accept kinetic energy. But in this model, this energy must be positive, becoming least in the "equipoise" compounds NaF, KCl, RbBr, and CsI. It is very doubtful if the source of the negative values for z in the preponderance of these expressions can result from faulty data.

Table 2

Empirical Constants in Expressions Relating Atomic Densities and Melting Points to Z, W, and mf for the Monohalide Salts

Atomic Density		x	y	yz	z	LogC	-x/(y+yz)
I-A	Chlorides	-15.371	13.978	-.523	-.0374	2.02604	1.1424
	Bromides	-6.186	5.235	.0747	.0143	-.05202	1.1649
	Iodides	5.935	-4.570	.2062	-.045	1.02250	1.3599
	Fluorides	9.762	-12.587	3.960	-.3146	5.35856	1.1316
I-B	Chlorides	1.747	-3.605	2.087	-.5789	2.78828	1.1506
	Bromides	6.069	-5.660	.013	-.0026	1.98636	1.0747
	Iodides	10.328	-9.570	.315	-.0329	2.54634	1.1160
		(11.216	-10.375	.420	-.0405	2.61314	1.1267)
Melting Point							
I-A	Chlorides	5.596	-5.242	.157	-.0300	4.18948	1.1006
	Bromides	3.368	-3.127	-.011	.0035	3.73829	1.0733
	Iodides	7.331	-7.094	-.072	.0102	5.27395	1.0229
	Fluorides	1.898	-2.066	.264	-.1280	3.73739	1.0534
I-B	Chlorides	3.353	-5.577	2.094	-.3754	6.21451	0.9627
	Bromides	12.302	-12.334	.194	-.0157	7.19884	1.0133
	Iodides	6.963	-7.754	-.309	.0398	7.33380	0.8637

Cursory examination of the above expressions indeed shows a trend in the values for x and y with regard to the atomic density equations for both A and B halides, and clearly this trend does not permit consideration of the fluorides as preceding the chlorides. Unfortunately, no similar trend is observed for melting points.

Were all z values of the same sign a simple remedy could be found. That they are not demands that a more acceptable form be used for describing the change in mass-momentum resulting from the presence of widely dissimilar masses.

Some foreshadowing of a probable cause can be seen in the PE values of Table 1; of the halite structures, nearly all are within one percent of the ideal 52.37 value. The exceptions are overpacked LiI and very much underpacked CsF, and without further evidence one might suggest that these are opposite ends of the spectrum of permitted radius ratios. But NaF is also significantly overpacked, yet lies near the center of the range of radius ratios[1].

It was not until comparatively recently that the atomic masses were given credence in such inquiries. Taking the heavier atom as dominant in determining permissible frequencies, one sees that in LiI and CsF this dominance is in one the halogen and the other the metal, and since the packing efficiencies differ on opposite sides of the ideal, one is forced to recognize the need for explaining them and compensating for them.

In the sense that the atomic density is itself based upon the real solid rather than an ideal model, its value in practical usage would indeed be enhanced by an example of deriving from it information needed to reconcile some of the discrepancies noted. The alkali halides provide an unequalled opportunity for such an example.

It had been recognized[1] that in few of the alkali halides was the radius ratio R_M/R_X small enough so that overlap repulsion between anions is the principal determinant of interatomic distance; it appears from the PE data that only in LiI and perhaps LiBr doeas this situation exist. In the remaining monohalides, the radius ratio approaches and may perhaps exceed unity so that AD_c is determined in the halite structure by the attraction-repulsion balance in the direction of the cubic axis.

It has been amply demonstrated, however, that the AD_c values observed do not accord with the theory that the atoms are, for a given element, spheres of inalterable dimensions; the effective radius of Na, for example is changed if it is moved from an array of Cl atoms into one of I atoms.

The usual and cogent arguments regarding electronegativity and changing ionicity-covalency in the salt are inappropriate in this study, the purpose of which is not to explain by theory but to demonstrate factual relations. It suffices here to note that a mathematical relation can, for example, be precisely drawn to describe N in terms of four constants for a given subgroup of four species, but unless this expression also permits equally accurate correlation with another, or with a fifth subgroup member, its development is merely an exercise in arithmetic.

Since atomic density changes as a function of temperature, it is not perhaps surprising that such correlation can be observed between the melting point and Debye temperatures. In such cases, the atomic density is merely used as an intermediary characterizing parameter to be excluded later. It seems highly desirable to utilize some other property, obtained, like N, at room temperature. For the example shown here, this property will be the elastic constant E.

RELATIONS WITH E, MP, AND N AND x, y, and z FOR SELECTED HALIDES

A substantial portion of the illustrative example to be described here was, because of its speculative nature, performed without charge to this project; it is reported in some detail here to illuminate the kind of approach which ought to be carried out by computer means.

It is clear from the expressions of Table 2 that both Z and mf are inadequate to the task. Each will be briefly discussed.

ATOMIC NUMBER AND THE PERIODICITY FUNCTION AS PARAMETERS.

Scanning the Z values given in Table 1 one observes that the difference in Z between fluoride and chloride is always 4, half that of the remaining differences. Yet the difference in N, MP, and E between fluoride and chloride is usually most impressive of the series, and as a result the value of x (and y since W bears a rough relation to Z) is most strongly affected by the property of the Li salt.

The usefulness of n, here termed the periodicity function for an element or salt, was demonstrated in the discussions regarding the Hume-Rothery expression and extending a modification of it to the melting and boiling points of the inert gas elements and the elastic constant c_{11} of the body-centered cubic transition metals in Report No. 1.

In the fully ionic fluorides, the ion can be described as one which comprises the characteristic nucleus of the metal or halogen external to which is the typical electronic configuration of the inert gas. In the dissimilar pair Na-F this configuration is that of Ne, in K-Cl it is that of Ar, in RbBr that of Kr, and in CsI that of Xe.

Since these "equipoise" compounds not only are distinguished by commonality of inert gas configuration but nearly the same atomic weight for each constituent, one might expect them to differ in some properties quite markedly from the remaining halides, but apart from the high melting point of NaF and the low density of KCl, such differences are not observed. The answer might lie in the fact that the balance between attractive and repulsive forces are here most nicely observed.

It follows that instead of the atomic number Z, a better yardstick would be a simple periodicity function such as n . Earlier work suggested simple integers 1, 2, 3.. for Ne, Ar, Kr... and these have been used somewhat arbitrarily here. As a result the value of the yardstick between Ne and Ar has been increased to equal that for Ar-Kr.

The objection that on this scale there are a different number of elements intervening is not particularly important so long as the atomic weight W is included as a characterizing parameter. One can either regard, among the alkali halides, the value of n for KBr as 2.5 because it is a Law of Mixtures mean for the n values of Ar and Kr or use the more complex but more universally applicable basis of counting the change in n in units of 1/18, so that KBr involves the mean of the sum 2.0555.. for K and 2.94444.. for Br.

For Li and Na, there is, and until future attention can be properly paid to it, some doubt as to the proper values for n ; it should be quite clear that He cannot have the value of zero and hence that values for Na and Li should be slightly higher than shown. At this time, however, one can accept the small penalty of absolute inaccuracy for the reward of being able to accept Na salts into the alkali metal subgroup and fluorides into the halogens.

In order to do this, one must simultaneously choose and test some expression of the mass factor which will be more sensitive than mf as the energy-absorbing mechanisms related to dissimilar masses.

THE MASS FACTOR AS A PARAMETER

It has become quite clear that in compounds one cannot merely choose the difference between atomic masses as a guide to the mass momentum effect; the difference is itself an expression of mass and therefore affects the exponent y; moreover, where the difference is very large (as with LiI or CsF) it is clear that an inordinate weight for it is implied in the derived equation.

It was accordingly decided to utilize a dimensionless term f to replace mf in the general expression and inquire into the equations of certain subgroups among the alkali metal halides. In order to clarify doubts as to the identity of the lighter atom while under the constrictions of logarithmic expression, the first step was undertaken because of the following facts:

In all Li salts, W_{Li} is less than W_X (the hydride excepted)
In all iodides except CsI, W_M is less than W_I,

and these two subgoups can therefore represent those salts in which the cation is the lighter. Also,

In all Cs salts, W_{Cs} is more than W_X , and
In all fluorides except LiF, W_M is more than W_F , and these two subgroups can be used to represent salts with heavier cations. Since, in general the heavier atoms are also larger, the latter group also represents those of larger radius ratio R_M/R_X.

The simplest means for describing the factor f in dimensionless terms is: $f = (W_X - W_M)/ W$;these are given in Table 1 without sign. For the general equation: $\text{Log } P = x \text{ Log } n + y \text{ Log } W + yz \text{ Log } f + \text{Log} C$, the values shown below have been derived.

		x	y	yz	Log C	z
Li salts	(N) -	1.94586	0.515120	0.980563	-0.04042	1.90356
	(E) -	2.64884	.664625	1.43909	.35566	2.16527
	(MP)-	0.83978	.151898	.68765	2.68765	4.52707
Iodides	(N) -	8.93259	29.18952	5.95098	-51.54422	.20387
	(E)	-18.19921	11.44106	56.328197	-99.11624	.20311
	(MP)-	8.93259	8.04043	37.67939	-65.33441	.21339
Cs salts	(N)	0.44166	0.682411	0.042704	1.55381	- .06258
	(MP)-	0.31509	.174708	.003949	2.77706	.02260
Fluorides	(N) -	4.04921	.988590	.679624	.08664	.68747
	(MP)-	0.09181	-.147838	.002303	3.29505	- .01558

In the metal-lighter (and smaller) salts the signs of x, y, yz and of course z are consistent throughout, and the exponents for E are larger than for N and MP in the Li salts, but this applies only to x and yz in the iodides. Values of z vary widely in the Li salts and are nearly constant in the iodides.

In the metal-heavier salts (for which data for E are lacking), the consistency in sign is lacking, although all yz values are positive throughout. Exponent values are much more consistent among the Cs salts than the fluorides.

From these data, one can justify the expectation that the magnitude of the mass factor effect will differ between metal-light and metal-heavy salts. An attempt was made to "predict" the missing value of E for CsF through its value of y Log f in the fluorides expression for N and its value of z from the Cs salts expression; the value is 2.568 GPa . An attempt to "predict"the value of N for CsI in a similar manner failed.

The values appropriate to all of these compounds appear to depend upon both better values for n and for f. A final attempt to initiate this was made in the following way.

EXPRESSIONS FOR MP AND N IN THE EQUIPOISE SALTS.

Thus far, each subgroup has consisted at most of four species, and one must rely on inspection of the completed expressions to estimate their credibility. With serious doubts about the values of f for all salts and of the appropriate values of n for Li (and perhaps Na) salts, a sizable regression program would be required for any but a serendipitous inquiry.

The matrix diagram shown here suggests a method of preliminary inquiry. The normal matrix of five metals and five halogens has been modified by including LiH as the only "halide" in which that metal is the heavier. Two values for f are shown for each salt, the first being that of Table 1, the parenthetical value being obtained from: $f = (W_X - W_M)/ W_l$, W_l being the atomic mass of the lighter element.

	Li	Na	K	Rb	Cs
H	-1.4926 (-6.0825)				
F	.9299 (1.7379)	-.1901 (-.21009)	-.6920 (-1.0582)	-1.2726 (-3.4988)	-1.4997 (-5.9956)
Cl	1.3452 (4.1092)	.42651 (.54212)	-.0979 (-.1028)	-.8273 (-1.4108)	-1.1577 (-2.7488)
Br	1.6804 (10.5159)	1.1063 (2.4758)	.6858 (1.0436)	-.06725 (-.06959)	-.4980 (-.6632)
I	1.7926 (17.2855)	1.3864 (4.4200)	1.0578 (2.2456)	.3902 (.4848)	-.04619 (-.04729)

The contours of this matrix can be described as being dominated by a trough of lowest values for the five "equipoise" salts LiH, NaF, KCl, RbBr, and CsI. From this trough the values of f rise in moving toward LiI and also rise (negatively) in moving toward CsF.

The addition of LiH to the series does not improve the credibility of the Li salts expressions given earlier, since it is a metal-heavier compound. It can, however, be examined as a member of the equipoise salt series in the following way. The expressions for these using the normal values of f are:

Log N = -2.753604 Log n + .597441 Log W - .979611 Log f -.59278

and Log N = -2.886996 Log n + .627678 Loh W -1.01650 Log f' -.615256

when the values for f' are the parenthetic ones shown above. One can then solve for the value of n for LiH assuming other n values are as shown in Table 1. It will be quite clear that n_{He} cannot be zero; the above simple approximation suggests n_{LiH} to be 0.1772 for the first, and 0.1828 for the second. Note that these values would be slightly higher if n_{NaF} is slightly greater than unity, as suggested by the inert gas solids relation.

At this time, one can merely find some satisfaction in that the suggested values for n_{LiH} are reasonable. A greater degree of confidence must await the final selection of the term f.

In the above matrix, it will be observed that the range of f' (from highest to lowest value regardless of sign) is far greater for Li than for the remaining salts. Perusal of the data for N, MP, and E in Table 1 shows a similar trend, and it appears that the use of f' values will permit more tractable expressions to be derived.

Even with Z and f values, however, the mass factor term suffices to reconcile all observed anomalies. The very small difference in MP for KBr and KI has been noted. In the form:

	MP =	C +	Z^x x	W^y x	f^{yz}	if z
KF	1154	680.6	1652.4	2791	1.0035	.002265
KCl	1048	"	3353.2	5074	1.0161	"
KBr	1003	"	10477	15285	1.0069	.004812
KI	996	"	23421	33505	1.0232	"

which suggests that the value of z for the metal-lighter salts is of the order of twice as effective as that for the metal-heavier salts.

Such observations, however, must be subjected to closer scrutiny among a number of alloys and compounds. Within carefully restricted subgroups, however, one can begin to pursue the ultimately rewarding course of eliminating unknown or difficultly measurable parameters. In the two similar equations for the equipoise compounds on the preceding page one derives simply: $\text{Log } N = .7888 \text{Log } n - .2055 \text{ Log} W + .00409$; it is these simpler expressions which will serve to determine both ideal behavior and the causes for deviation from it.

SUMMARY

Using the monohalide salts with particular emphasis on the halides of the alkali metals, the unsatisfactory usage of atomic number Z as a principal determinant in compounds has been tentatively replaced by a "periodicity factor" n which has, for the alkali halides, a value equal to the mean n-values of the inert gas configurations represented by their ions. (n for the inert gases is one less than the principal quantum number of the outermost filled shell). By comparison with LiH, a tentative value for n_{He} of about 0.18 was derived.

Using the dimensionless mass factor : $f = (W_X - W_M) / W$ and taking care to treat separately those subgroups in which the metal atom is lighter (Li salts and iodides except CsI) and those in which it is the heavier (Cs salts and fluorides), mathematical expressions of the form: $P = \text{Log } n^x + \text{Log } W^y + \text{Log } f^{yz}$ were carried out. Large and apparently meaningless variations in the several equation parameters which had been apparent with Z and mf terms were found to be considerably reduced, and it is now believed possible to develop an expression for f in which the values of z will be substantially constant for a given property. These expressions, since they utilize the periodicity factor rather than Z, permit the subgrouping of Na with the I-A metals, F with the remaining halogens, and do not require (at least in these salts in which CsCl, CsBr, and CsI exhibit a structure quite different from the remaining ones) correction to a common coordination.

Anomalies such as the overpacking of LiI and CsF were found to relate to extremes in metal-lighter and metal-heavier compounds, each of which will probably require a characteristic value of z.

Of the "equipoise" compounds in which the constituent atoms are almost the same in atomic mass, NaF and LiH demonstrate (by melting point and slight overpacking) that the greatest sensitivity of the mass factor to the mass ratio itself occurs when such a balance is nearly achieved; at the same time this sensitivity is greatly lowered if either atom is very heavy. Accordingly, the atomic weight W must continue to be included in the expression.

Trials for more sensitive forms of the mass factor f have included one one in which the mean atomic weight W is replaced by that of the lighter component.

In view of the necessity for regarding every property value as precisely known, expressions were, where data permitted, drawn for the atomic density N, the principal elastic constant E, and the melting point MP. As expected from their common temperature of measurement, expressions for N and E were most nearly the same. Although some of these preliminary expressions are formidable in appearance they can easily be modified and combined to produce accurate, if not yet generalizable, relations among a few of the important properties of a material. To the extent that some of these relations clearly indicate invalid data points they are immediately useful.

CONCLUSIONS AND RECOMMENDATIONS

As this largely exploratory phase approaches its end one observes that the atomic density N is indeed a useful and tractable characterizing parameter. Like all such it cannot stand alone. Among the elemental solids studied it has proved invaluable in the discovery that a small but real (1-6%) influence on such properties as density, melting point, Debye temperature, and elastic constants is exerted by the proportion and masses of their isotopic contents, and this influence in polyisotopic elements is inadequately represented by a Rule of Mixtures solution. That different isotopes of an element will exhibit measurably different properties has long been known and is particularly apparent in isotopes of the lighter elements. That interactions among them apparently suffice to account for appreciably larger differences is a novel conclusion, unexplainable in terms of spin parameters or electronic configuration in the heavier elements.

If such effects are measurable in polyisotopic elements they are surely notable in compounds. An investigation of a number of monoxides followed by a more detailed study of the alkali halides confirm this conclusion, and suggest that this approach be used for a wider range of well-characterized compounds, a few alloys, and involving other properties.

The choice of elemental subgroups used in the derivation of empirical compounds was dictated by the Periodic Table, so that only in the III-A elements and lanthanons was it possible to extend the subgroup population above the minimal number of four. A modest modification of the Table was shown capable of achieving credible expressions for the I-IV-A and -B elements, but it was noted that this change should not persist into ionic compounds in which the principal bonding mechanism is electrostatic attraction. Finding that it did indeed persist, the writer perceived that the problem might well lie in the selection of the atomic number, which describes the total electron population, rather than the periodicity, which describes the recurrence of valence. A number of earlier studies had suggested that this periodicity factor was well served by consecutive integers for elements heavier than Cl. It may be concluded, within the limitations of a single study of the alkali halides and LiH, that either the periodicity factor, n, or a modification of the atomic number Z to accord with the number of external electrons of the He and Ne "cores" can be used to develop exact expressions. The latter method had already been applied to post-lanthanon metals with good success.

The body of knowledge of materials properties being greatest at room temperature and atmospheric pressure, virtually all atomic densities considered thus far relate to these conditions. The writer makes no claim to superior judgment in his selection among data available in compendia and selected papers. It is a sincere tribute to note that most reported data have been more accurate than generally supposed. This appears also to be true of many real density values, a large number of which have been irremediably rounded off before publication.

Recommended future work includes:

1. Continuation of the detailed study of the alkali halides, broadened to include NaH and the halides and hydride of ^{6}Li (or Li relatively high in this isotope). In addition to referee-quality densities and observed interatomic distances, the following property data are needed: RT bulk modulus and elastic constants, coefficient of thermal expansion, dielectric constant, refractive index and transmission limits; real density and lattice dimensions at elevated temperatures to melting point.

2. Initiation of a study of the sesquioxides, particularly those of the lanthanons. Principal data requirements include real density, lattice dimensions, melting point, and refractive index. Single-crystal data are preferred, but hot-pressed specimens can be used if stoichiometry is preserved. Over thirty of these oxides exist.

3. Preliminary study of the transition metal oxides, density, melting point, and RT bulk modulus being the minimal data sought.

4. Several alloy specimens of known composition and density and melting points from each of two systems: a binary alloy which conforms to Vegard's rule and another (preferably containing a common element with the first) which does not. Suggested are the Cu-Pd and the Cu-Ni-Zn systems.

5. In this and earlier reports the writer has suggested that a simple computer program be developed and used to generate expressions which can be used to test values for n and f. Once these are known the work can be carried out with greater confidence, and the the mechanism and meaning of them be attacked by theoreticians.

Respectfully submitted

SW Bradstreet

Pricipal Investigator