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Effective ionic charge and bulk modulus scaling in rocksalt-structured rare-earth compounds

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The bulk moduli of rocksalt-type divalent and trivalent rare-earth (R) monochalcogenides exhibit a linear relationship when plotted on a log-log scale against the unit-cell volume, but fall on two distinct straight lines according to the effective valence product of the compound. By comparing the bulk modulus ratio of the R monochalcogenide to the alkali halide at the same volume, we have estimated the effective ionic charges. These charges are found to be 1.7 ± 0.03 and 1.85 ± 0.05 for the R^{2+} and R^{3+} compounds, respectively, as against 2 and 2.45 expected from their valence products. The behavior of NaCl-type Ce monopnictides is somewhat anomalous.

INTRODUCTION

The interatomic potential for an ionic compound consists of a repulsive term due to the overlap interaction and an attractive Coulomb term. This suggests a simple scaling behavior for the bulk modulus B_0 as a function of the equilibrium interionic distance within a given class of compounds. Experimentally, Anderson and Nafe[1] first demonstrated that B_0 scales with the specific volume for related compounds. Accordingly, the alkali halides, some fluorides, and several chalcogenides for which data were available exhibited a straight-line relationship in a plot of $\ln B_0$ vs $\ln V_0$, but sorted out according to the valence. A similar scaling was found for divalent rare-earth (R) monochalcogenides[2] but no further interpretation was attempted. In the present study, we compare the bulk modulus of divalent and trivalent R monochalcogenides and some monopnictides, all of which crystallize in the rocksalt structure. The outstanding advantage of this isostructural sequence[3] is that the scaling predictions can be tested not only with respect to the interionic distance, but also with respect to the variation of the ionic charge: The monochalcogenides of the divalent R are semiconductors,[4,5] whereas the ones of the trivalent R are metals.[4,5] In turn, we can derive "effective" charges from the difference between the experimental and the theoretically scaled values of B_0.

BULK MODULUS DATA

The pressure-volume relationship for divalent rare-earth monochalcogenides has been extensively investigated by high-pressure x-ray diffraction[2,6]

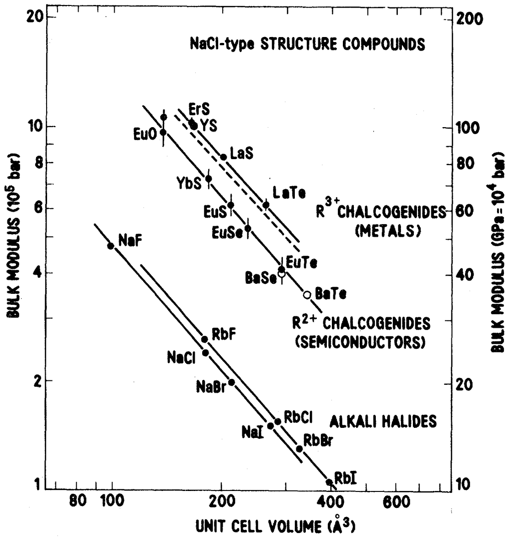

FIG. 1. Bulk modulus scaling behavior with unit-cell volume for the NaCl-structured divalent and trivalent rare-earth monochalcogenides. The plot for the alkali halide series is also shown as a reference for univalent series. The R^{3+} monochalcogenides are metallic and hence the dotted line below the R^{3+} line represents the correction for the free-electron contribution to the bulk modulus.

TABLE I. Lattice parameter and the bulk moduli of compounds appearing in Fig. 1. NM denotes values from our new measurements of Δl with the strain-gauge technique. $B_0' = 5.4 \pm 0.2$ for ErS and LaTe.

Substance	Lattice Parameter a (Å)	Bulk modulus B_0 (kbar)	Reference
EuTe	6.60	400±50	2,6
EuSe	6.19	520±50	2,6
EuS	5.97	610±50	2
EuO	5.14	900±100	6,7
		1100±50	2
YbS	5.68	720±50	2
BaSe	6.62	396	1
BaTe	6.99	341	1
ErS	5.43	1015±10	NM
LaS	5.85	836[a]	10
LaTe	6.42	606±20	NM
YS	5.49	998[a]	10
NaF	4.62	486	1
RbF	5.63	273	1
NaCl	5.627	252	1
RbCl	6.571	162	1
NaBr	5.96	211	1
RbBr	6.868	138	1
NaI	6.46	161	1
RbI	7.325	112	1

[a] Elastic constant from ultrasonic measurements.

and from this their bulk moduli B_0 have been evaluated.[2,6] Also, for many of the divalent and some trivalent rare-earth monochalcogenides and some trivalent pnictides elastic-constant data obtained from ultrasonic measurements[7–9] exist and from these their adiabatic bulk moduli are easily obtained.[9] Among the $R^{3+}X$ (X is a chalcogen) such data exist for YS and LaS.[10] To provide a wider range for comparison, we have determined the iosthermal bulk modulus of LaTe and ErS, employing a newly developed technique of length-change measurements.[11] This method uses an extremely sensitive strain gauge in conjunction with the Teflon-cell technique to generate hydrostatic pressure.[12] The sensitivity and the precision of the strain-gauge technique are sufficient to determine even the pressure derivative of B_0 (dB_0/dP) reliably.

In Fig. 1 the bulk modulus-volume relationship for $R^{2+}X$ and $R^{3+}X$ is presented for the specific log-log plot; for volume the unit-cell volume is used. In the same figure the log of B_0 against the log of V_0 for the Rb and Na halides are plotted. That the data in all cases fit a straight-line relationship and that the slopes for the three series are nearly identical is quite evident. The data used are given in Table I.

DISCUSSION

From the observed relationship between B_0 and V_0, Anderson and Nafe[1] proposed the empirical law that

$$\ln B_0 = -\ln(V_0) + \ln Z_1^* Z_2^* + \text{const} , \qquad (1)$$

where V_0 represents volume per ion pair, and $Z_1^* Z_2^*$ the effective valence of the cation and the anion. The above empirical equation is derivable from simple concepts of classical ionic crystal physics. One can predict a power-law relationship between r_0 and B_0 based on the ansatz for the interionic potential in an ionic solid.[13,14] One may write for the interionic potential

$$\phi(r) = -\frac{a}{r^m} + \frac{b}{r^n} . \qquad (2)$$

Minimizing the total energy with respect to the interionic distance r leads to the equilibrium separation r_0. With the Coulomb law for the attractive term, a further differentiation yields the bulk modulus B_0 at zero temperature and pressure

$$B_0 = \frac{n-1}{9} \alpha_M \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0} n_p r_0^{-4} , \qquad (3)$$

where Z_1Z_2 denotes the charges on the ions, α_M the Madelung constant, and n_p the number of ion pairs in r_0^3. According to (3), B_0 depends directly on the product of the charges and inversely on the fourth power of r_0, or equivalently $V^{-4/3}$. This is only true, however, if the exponent n of the repulsive potential was the same for the various values of r_0. Instead of b/r^n in Eq. (2) we may approximate the repulsion by an exponential form like e^{-r/ρ_0} and again derive the bulk modulus

$$B_0 \sim Z_1Z_2 \left[\frac{r_0}{\rho} - 2 \right] r_0^{-4} \; . \tag{4}$$

By fitting the two expressions (3) and (4) to the experimental data of r_0 and B_0 of the alkali halides, one finds that neither n in (3) nor ρ in (4) are constants within the series of alkali halides, but vary slightly with r_0. This is consistent with the observation in Fig. 1 that B_0 is proportional to $r_0^{-3,4}$, and not exactly to r_0^{-4}. We note in passing the r_0^{-5} dependence of B_0 for free-electron metals and covalent solids (see, e.g., Ref. 14).

The above principles are the basis for the straight-line relationships found by Anderson and Nafe in their $\log B_0 - \log(V)$ plots and the sorting out of the straight lines according to the effective valence product.

What is remarkable in Fig. 1 is that the data points for the $R^{2+}X$ and $R^{3+}X$ compounds fall on two curves, nearly parallel to the alkali halides, which means ionic binding dominates all these compounds. The $R^{2+}X$ compounds are semiconductors or insulators, while $R^{3+}X$ compounds are metallic with electronic densities between 1 and 3 $\times 10^{22}/\mathrm{cm}^3$. The electronic contribution to the bulk modulus can be estimated and the data corrected for it. We have done this by using the simple formula for free-electron compressibility $B_e \approx \frac{2}{3} n_e E_F$, where n_e is the electron concentration and E_F is the Fermi energy. The dotted line in Fig. 1 below the $R^{3+}X$ line represents the corrected line for the $R^{3+}X$ series. Such a simple way of accounting for the (small) electron bulk modulus appears justified since the electrons are occupying a free-electron-like part of the *s-d* conduction band.

While the slopes are nearly the same for the different lines, they sort out according to the valence product [see Eq. (1)]. The alkali halides serve as a series to define the line for $Z_1 = Z_2 = 1$. The square root of the ratio of the bulk modulus of the $R^{2+}X$ to that of the alkali halide at the same volume is therefore a measure of the effective charge.[1] This ratio is between 2.8 and 3 for $R^{2+}X$ and 3.4 and 3.7 for $R^{3+}X$, depending upon whether the Rb halides or the Na halides are chosen to represent the alkali halide line. Na halide probably represents the alkali halide line better. If B_0 and the valence product of the alkali halides are normalized to 1, we find the scaling parameters shown in Table II for the $R^{2+}X$ and the $R^{3+}X$. The numbers in column 3 (B_{expt}) may be regarded as the effective-charge product for the series with reference to the alkali halide. From this, the effective change (Z_{eff}) of the ion is obtained by taking the square root, and this is shown in column 5 of Table II. The effective charges thus obtained are lower than the nominal ones shown in column 4 in Table II. The last column indicates the deviation of the effective charge from the nominal value. While calculating the elastic constants of $R^{2+}X$ compounds using the Krishnan-Roy theory[15] for ionic crystals, Sirdeshmukh[16] also found that substantially reduced ionic charges must be used to get better agreement with experimental values. According to the latter, reduced charges between 1 and 1.5, depending on the chalcogen, were found to give better agreement. Thus the results strongly suggest the presence of covalent bonding (directional forces) in R monochalcogenides with the NaCl-type structure.

The existence of noncentral forces in rare-earth monochalcogenides is reflected also in the deviation from Cauchy relations, e.g., $c_{12} \neq c_{44}$. We expected a screening of the cationic charge by the conduction electrons in $R^{3+}X$ compounds. That

TABLE II. Valence product, bulk modulus ratios, and effective ionic charges. B is the bulk modulus of the R monochalcogenide and B_A is the bulk modulus from the alkali halide line.

Compounds	Nominal Z_1Z_2	B_{expt} B/B_A	$\sqrt{Z_1Z_2}$	$\sqrt{B/B_A} = Z_{\mathrm{eff}}$	$\frac{Z_{\mathrm{eff}}}{\sqrt{Z_1Z_2}}$
Alkali halides	$1\times1=1$	$\equiv 1$	1	$\equiv 1$	1
$R^{2+}X$	$2\times2=4$	2.8–3	2	1.67–1.73	0.85
$R^{3+}X$	$3\times2=6$	3.4–3.7	2.45	1.84–1.91	0.77

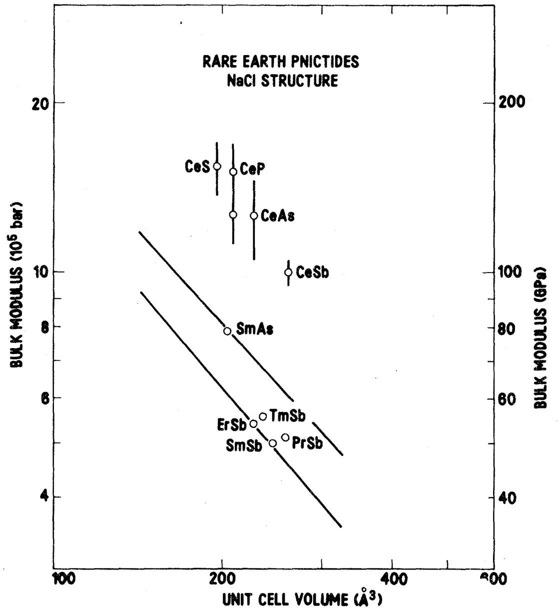

FIG. 2. Bulk modulus vs unit-cell volume (log-log scale) for the NaCl-structured rare-earth monopnictides. The line through ErSb and SmSb and the line through SmAs are, respectively, from the divalent and trivalent rare-earth monochalcogenides. The data of Ce pnictides have a large uncertainty, but the behavior is quite anomalous.

there is some screening is reflected by the numbers in the last column in Table II. The $Z_{\mathrm{eff}}/\sqrt{Z_1 Z_2}$ of 0.85 for $R^{2+}X$ and 0.77 for $R^{3+}X$ indicates such an effect is present but is not as striking as one might expect.

In Fig. 2, we have plotted the bulk moduli for several rare-earth pnictides for which elastic-constant data were available from the literature.[9,10,17] It is evident that the behavior of pnictides does not fall in line with the rare-earth chalcogenides. The nominal valence product for these semimetallic compounds would be 9, which would lead to an ionic charge of 3. The values of effective charges derivable from the curves would be much lower. The cerium pnictides are anomalous. Despite the fact that there is a large uncertainty in their B_0 values, the Ce pnictides are out of line with the others. Cerium and cerium compounds are found to be anomalous in their properties compared to the rest of the trivalent rare earths. Whether the present situation has anything to do with the tendency of Ce towards quadrivalency is hard to judge. One might invoke the particular instability of the $4f^1$ configuration and the proposed f-p hybridization[18] to account for the anomalies.

Anderson and Nafe found that oxides were completely out of line with the other systems. In the plots for oxides, the crystal structure was ignored. We believe that it is not correct to compare oxides having different structures, or compounds with different structures and moleculear formulas. The first reason is that the repulsive potential due to the overlap interaction depends on the number of neighbors; the second one is that the magnitude of the electrostatic interaction depends on the geometrical arrangement of the charges and manifests itself in Eqs. (2) and (3) in different Madelung constants.

The plot presented in Fig. 1 is useful to identify a mixed-valent R monochalcogenide provided the bulk modulus is known. Also, the P-V relationship for any R monochalcogenide can be generated through an equation of state, with B_0 read from Fig. 1 and B' assumed. This will be particularly useful if a compound can be driven from one valence state to another by pressure and a comparison of the pressure-volume behavior is to be made with that of the two end valence state members.

SUMMARY AND CONCLUSIONS

We note the following.

(1) The rare-earth monochalcogenides are an ideal series for checking the bulk modulus scaling with specific volume and ionic charge predicted by general theories of ionic compounds, and first discovered by Anderson and Nafe. Both the semiconducting $R^{2+}X$ and metallic $R^{3+}X$ (X is a chalcogen) exhibit a linear relationship between the log of B_0 and the log of V_0. Furthermore, the slope obtained agrees with that of the alkali halides, indicating that the compounds are predominantly ionic. The trivalent RX therefore is justifiably termed "ionic metals."

(2) The compounds sort out according to the effective-charge product $Z_1 Z_2$ of the constituent ionic species.

(3) From the above feature, the effective charges on the ions can be estimated by comparing the B_0 for the $R^{2+}X$ or $R^{3+}X$ with the alkali halide at the corresponding V_0. The charges thus found are ~25% lower than the values expected from the nominal valence product.

(4) The rare-earth pnictides which are nominally trivalent behave quite differently and do not fit any pattern. Among these, some fit the $R^{3+}X$ line, some $R^{3+}X$, line, while Ce pncitides are completely out of line. However, their effective charge

is markedly smaller than 3.

(5) Our general conclusion is that it is more meaningful to compare isostructural sequences rather than general classes with different molecular formulas and different structures.

(6) Figure 1 is useful to identify mixed valent regimes and to generate the pressure-volume behavior of R chalcogenides.

Note added in proof. Ybo (Ref. 19) with $B_0 = 1300 \pm 100$ kbar and a unit-cell volume of 116.2 Å^3 fits in well on the plot in Fig. 1 for the R^{2+} chalcogenide line.

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