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A Study on Mixed Halide Compounds MFX (M = Ca, Sr, Eu, Ba; X = Cl, Br, I)

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MFX (M = Ca, Sr, Eu, Ba; X = Cl, Br, I) compounds have been prepared by solid-state reaction. Lattice parameters and X-ray diffraction patterns are presented for these compounds, which are all isostructural with tetragonal PbFCl. Attempts to synthesize solid solutions of Sr(Eu)FCl and of MFCl compounds with several rare earth oxychlorides are reported. The crystal chemistry of MFX, MHX, and $LnOX$ compounds is briefly discussed in comparison, and the observed c/a ratios are interpreted on the basis of electrostatic calculations.

Introduction

Alkaline earth fluorochlorides and fluorobromides crystallizing in the PbFCl (EO_1) structure type have long been the object of investigation, and early work dates back as far as 1894 (*1*). Preparations and properties of such mixed halide compounds and even complete phase diagrams of MF_2–MCl_2 systems have been reported (*2*). Some of these compounds have attracted interest as host crystals for epr measurements on defect centres and for luminescence experiments. A systematic study, however, of all possible alkaline earth fluorohalides and the determination of their lattice parameters has met with little interest. In the attempt to prepare alkaline earth subhalides Ehrlich et al. (*3–5*) discovered the hydridehalides, and in the course of their work they have published structural data of all respective MHX (X = Cl, Br, I) compounds. During our investigations on high temperature polymorphisms of AB_2 compounds we discovered that alkaline earth halides or even their hydrates reacted with Voltalef,[1] a fluorocarbon high-vacuum grease used for an easier preparation of the high-temperature Guinier samples, to form fluorohalides. Later this method was used to define the stabilities of such compounds and the preparative conditions for normal solid-state reactions. This paper presents the conditions of preparation and the lattice parameters of the fluorohalides of the alkaline earths and of divalent europium. The existence of some of these compounds is reported for the first time.

Experimental Procedures and Results

Sample Preparations

For the solid-state preparations two different methods were examined: (*a*) the reaction of dehydrated halides with the corresponding fluorides, and (b) the fluorination with MnF_2, which several authors have used successfully (*6*). To avoid the formation of oxide impurities, the waters of hydration were removed carefully by heating the hydrated halides under vacuum slowly to 300–350°C in the course of 6 to 12 hr. This method of dehydration was also used for the preparation of $EuCl_3$ and $EuBr_3$; high vacuum and even slower heating to 350°C within 24 hr yielded samples with no detectable oxyhalide contamination. However, partial reduction due to the decomposition

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[1] Manufactured by Ugine Kuhlmann, Société des Usines Chimiques, licence KEL'F = 3M.

to $\mathrm{Eu}X_2 + \frac{1}{2}X_2$ is possible under these conditions (*7*). The trihalides were subsequently reduced in a flowing atmosphere of H_2 at 600°C for $\mathrm{EuCl_2}$ and $\mathrm{EuBr_2}$ and at 900°C for $\mathrm{EuF_2}$, using platinum crucibles in the latter case. $\mathrm{EuI_2}$ was prepared in a similar way by slow thermal decomposition of the $\mathrm{EuI_3}$-hydrate under high vacuum (*8*). With the exception of $\mathrm{EuF_2}$, the crude dihalides were then distilled under a dynamic high vacuum at temperatures between 700 and 900°C. Again X-ray powder patterns showed only one phase present. Since all dihalides with the exception of the fluorides are extremely hygroscopic, they were subsequently handled in inert gas atmospheres.

In all cases, the fluorohalides are found to form at quite low temperatures. Sintering of the components $M\mathrm{F}_2$ and MX_2 under argon between 600 and 750°C for 3 to 5 hr is sufficient. At higher temperatures the fluoroiodides decompose, and under such conditions it is advantageous to use closed crucibles or an excess of MX_2 to ensure a stoichiometric reaction, which may otherwise be incomplete due to the evaporation of some dihalide. The existence of CaFI can be proved only by an extended study of the $\mathrm{CaF_2}$–$\mathrm{CaI_2}$ phase diagram. No reaction is observed when sintering the components at temperatures up to 450°C. At higher temperatures, $\mathrm{CaI_2}$ separates from the bulk material in soft spherical drops without recrystallizing, as though it were a liquid with a high surface tension. This could be due to a miscibility gap in the melts.

The fluorination of the dihalides with $\mathrm{MnF_2}$ according to the reaction

$$\mathrm{MnF_2} + 2MX_2 \rightarrow \mathrm{Mn}X_2 + 2M\mathrm{F}X$$

is only possible at high temperatures, where the manganese dihalide formed in the reaction is removed by sublimation, or in those cases, when it can be washed out with water and ethanol without decomposition of the fluorohalide. Fluorinating agents probably offer a method for the preparation of CaFI. However, at temperatures where $\mathrm{MnF_2}$ reacts, $\mathrm{CaI_2}$ is directly transformed to $\mathrm{CaF_2}$ with the remaining iodide again separating from the solid phase. It is only in high-temperature Guinier experiments, where the fluorination was achieved by the Voltalef grease, that we observed the formation of an intermediate

TABLE I

LATTICE PARAMETERS OF $M\mathrm{F}X$ COMPOUNDS

	a	*c*	*c*/*a*	*V*
CaFCl	3.894(3)	6.809(6)	1.749	103.25
CaFBr	3.883(1)	8.051(3)	2.073	121.39
[CaFI	4.29	8.70	2.028	160.11]
SrFCl	4.129(2)	6.966(4)	1.687	118.76
SrFBr	4.218(2)	7.337(5)	1.739	130.54
SrFI	4.253(2)	8.833(7)	2.077	159.77
EuFCl	4.118(2)	6.971(3)	1.693	118.21
EuFBr	4.219(2)	7.312(5)	1.733	130.15
EuFI	4.249(2)	8.732(4)	2.055	157.65
BaFCl	4.391(3)	7.226(4)	1.646	139.32
BaFBr	4.503(2)	7.435(4)	1.651	150.76
BaFI	4.654(3)	7.977(5)	1.714	172.78
EuFCl				
Lambrecht (*14*)	4.127	6.984	1.692	118.95
Tanguy (*19*)	4.075(6)	7.080(8)	1.737	117.57

mixed halide phase in the temperature range between 350 and 400°C. The powder diagram can be indexed on the basis of the lattice parameters given in Table I. They were determined at room temperature after cooling down the sample, and they seem to prove the existence of a PbFCl-type compound since the respective extinction rules also hold. We have not been able, however, to ascertain the exact chemical composition of these Guinier samples, and care should be taken in the interpretation of these data.

MFX compounds with large cations, M, and small anions, X, are fairly stable against water, e.g., BaFCl will only be decomposed by hot water—a method used to make finely dispersed BaF_2. However, the stability decreases with the size of the cation and with the increasing radius of the anion X, e.g., the fluorohalides of Ca are quite hygroscopic, yielding CaF_2 and hydrates of the Ca-halides which are themselves deliquescent. Therefore, tables of d values may contain the strongest lines of CaF_2 (e.g., ASTM 1-1100). The fluoroiodides quickly darken in air due to the formation of iodine.

X-ray Investigations

X-ray diffraction measurements were made using an AEG-Jagodzinski Guinier camera for those compounds which could be handled in air without hydration. For CaFCl, CaFBr, and all fluoroiodides we used a Simon-type Guinier camera (*9*), where the sample is sealed in a glass capillary. The photographs were read with a Hilger and Watts film reader and calibrated internally by adding Si to the samples. The lattice parameters (Table I) were refined by a least-squares procedure using the program GIVER (*10*).[2] Table II gives the d spacings for comparison with the calculated values. The roughly estimated intensities are severely affected by texture effects. Apart from the metrical changes, the variations of electron density on the M and X sites of the PbFCl-type structures are clearly reflected in the changing intensity features of the diagrams, which in their extremes can hardly be recognized as isostructural.

Experiments in the Systems MFCl–M′OCl

Since many rare earth oxyhalides exhibit the same layered tetragonal PbFCl structure as these MFX compounds, we tried to establish the existence of solid solutions of the fluorochlorides with rare earth oxychlorides. To facilitate the substitution we chose the lanthanide cations La and Yb, which match the ionic radii of the alkaline earth cations Sr and Ca fairly well. Various mixtures of SrFCl with LaOCl, EuFCl with EuOCl, and CaFCl with YbOCl, which does not crystallize in the PbFCl-type struture, were heated under argon at 700–900°C in alumina crucibles for up to 50 hr. Since small oxygen impurities could bring about significant F^- or X^- displacement by O^{2-} after such long reaction times, we used 5/9 pure Ar, which was additionally cleaned with P_2O_5 and BTS-catalyst to remove residual traces of water and oxygen. In the case of SrFCl–LaOCl, diffraction lines of the two components almost coincide. They might be interpreted as one set of lines if Debye–Scherrer or diffractometer techniques are used and the lattice parameters based thereupon might lead to the assumption of solid solutions. However, least-squares refinements using the two resolved patterns from Guinier photographs show no change of lattice parameters and indicate that solid solutions do not form on either side of the system SrFCl + LaOCl.

During the long reaction times of CaFCl + YbOCl and EuFCl + EuOCl we observed the slow decomposition of the oxyhalides to Yb_2O_3 and to unidentified products, respectively. We assume that the reaction is like that of the oxybromides of Sm, Eu, and Yb, and proceeds with the formation of intermediate Ln_3O_4X compounds (*11*). The existence of the corresponding oxychlorides has been established by the synthesis of Y_3O_4Cl (*12*) and Er_3O_4Cl (*13*). In both cases, least-squares refinements on the patterns of the remaining fluorochlorides showed no change in lattice parameters. Therefore, we cannot confirm the results of Lambrecht et al. (*14*), who claims to

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[2] All computations were performed at the computer center of the Karlsruhe University.

have observed solid solutions of EuFCl with LnOCl compounds.

EuFX Compounds and Solid Solutions Sr(Eu) FX

Eu compounds are often isostructural with the corresponding Sr compounds, since the Sr^{2+} and the Eu^{2+} cations are almost equal in size. Rare exceptions (e.g., the dichlorides) are attributed to the different cation polarizabilities, which stabilize different structure types. In the PbFCl-type mixed halide compounds the coordination spheres are not uniformly defined. Like the corresponding rare earth

TABLE II.A

CaFCl				CaFBr			
h k l	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o
0 0 1	6.809	6.82	20	0 0 2	4.025	4.04	35
0 0 2	3.404	3.411	10	1 0 1	3.498	3.499	35
1 0 1	3.380	3.382	30	1 0 2	2.795	2.799	100
1 1 0	2.754	2.753	90	1 1 0	2.746	2.748	60
1 0 2	2.563	2.565	100	0 0 3	2.684	2.681	40
1 1 1	2.553	2.555	60	1 1 1	2.598	2.599	30
1 1 2	2.141	2.143	80	1 1 2	2.268	2.269	65
1 0 3	1.961	1.963	20	0 0 4	2.013	2.012	20
2 0 0	1.947	1.948	85	2 0 0	1.942	1.941	60
2 0 1	1.872	1.870	10	1 0 4	1.787	1.786	70
1 1 3	1.751	1.752	8	2 0 2	1.749	1.748	20
2 0 2	1.690	1.690	10	2 1 1	1.698	1.696	20
1 0 4	1.560	1.563	20	1 1 4	1.623	1.623	35
2 1 2	1.550	1.550	60	2 1 2	1.595	1.595	75
1 1 4	1.448	1.449	40	2 0 3	1.573	1.573	25
2 1 3	1.382	1.382	10	1 0 5	1.487	1.487	10

TABLE II.B

SrFCl				SrFBr				SrFI			
h k l	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o
0 0 1	6.965	6.95	15	0 0 2	3.669	3.671	20	0 0 2	4.416	4.418	<5
1 0 1	3.551	3.550	100	1 1 0	2.982	2.986	90	1 0 1	3.832	3.832	10
0 0 2	3.483	3.479	10	1 0 2	2.768	2.770	100	1 0 2	3.064	3.061	100
1 1 0	2.919	2.915	80	1 1 2	2.314	2.316	65	1 1 0	3.008	3.007	70
1 1 1	2.692	2.689	5	1 0 3	2.116	2.115	10	0 0 3	2.944	2.947	<5
1 0 2	2.662	2.658	80	2 0 0	2.109	2.109	70	1 1 2	2.486	2.489	50
1 1 2	2.237	2.235	80	1 1 3	1.891	1.890	5	0 0 4	2.208	2.205	5
2 0 0	2.064	2.062	60	2 0 2	1.828	1.828	40	2 0 0	2.127	2.127	70
1 0 3	2.024	2.022	25	1 0 4	1.682	1.682	20	1 0 4	1.960	1.960	70
2 0 1	1.979	1.978	10	2 1 2	1.677	1.678	90	2 1 1	1.859	1.856	<5
2 1 1	1.785	1.784	50	1 1 4	1.562	1.563	15	1 1 4	1.780	1.780	45
2 0 2	1.776	1.774	25	2 1 3	1.494	1.493	20	2 1 2	1.747	1.747	90
2 1 2	1.631	1.631	50	2 2 0	1.491	1.491	45	2 1 3	1.598	1.601	<5
1 0 4	1.605	1.604	25	0 0 5	1.467	1.468	15	2 0 4	1.532	1.530	5
2 2 0	1.460	1.459	40	2 1 4	1.315	1.315	30	2 2 0	1.504	1.505	30
2 1 3	1.445	1.442	25	3 1 1	1.312	1.312	40	0 0 6	1.472	1.472	5

TABLE II.C

EuFCl				EuFBr				EuFI			
h k l	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o
0 0 1	6.971	7.00	20	0 0 1	7.31	7.34	10	1 0 2	3.051	3.045	70
1 0 1	3.545	3.546	100	1 0 1	3.654	3.649	70	1 1 0	3.008	3.004	20
0 0 2	3.486	3.482	30	1 1 0	2.983	2.980	90	1 1 2	2.479	2.475	20
1 1 0	2.911	2.912	80	1 0 2	2.763	2.761	100	0 0 4	2.183	2.183	40
1 0 2	2.660	2.659	70	0 0 3	2.437	2.439	<5	2 0 0	2.129	2.124	40
0 0 3	2.324	2.322	5	1 1 2	2.311	2.310	70	1 0 4	1.943	1.942	100
1 1 2	2.234	2.235	75	2 0 0	2.109	2.108	90	1 1 4	1.767	1.766	80
2 0 0	2.059	2.059	65	2 0 1	2.027	2.026	5	2 1 2	1.742	1.742	100
1 0 3	2.024	2.025	30	1 1 3	1.887	1.889	15	2 0 4	1.522	1.522	20
2 0 1	1.974	1.974	5	2 0 2	1.827	1.827	50	0 0 6	1.455	1.455	80
1 1 3	1.816	1.816	10	2 1 2	1.677	1.676	90	2 1 4	1.433	1.433	80
2 1 1	1.780	1.780	50	2 0 3	1.595	1.596	5	3 0 2	1.347	1.347	60
2 0 2	1.773	1.772	30	1 1 4	1.559	1.558	10	1 3 0	1.343	1.344	60
2 1 2	1.628	1.629	40	2 2 0	1.492	1.491	50	1 1 6	1.310	1.310	80
1 0 4	1.605	1.604	20	2 2 1	1.461	1.462	10	3 1 2	1.285	1.284	20
2 0 3	1.541	1.541	<5	2 2 2	1.381	1.380	40	2 2 4	1.238	1.237	10

TABLE II.D

BaFCl				BaFBr				BaFI			
h k l	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o	*h k l*	d_c	d_o	I_o
0 0 1	7.226	7.24	20	1 0 1	3.852	3.858	70	0 0 2	3.989	3.988	10
1 0 1	3.752	3.750	100	0 0 2	3.718	3.714	10	1 1 0	3.291	3.293	80
0 0 2	3.613	3.608	25	1 1 0	3.184	3.187	100	1 0 2	3.028	3.028	100
1 1 0	3.105	3.100	95	1 0 2	2.867	2.861	100	1 1 2	2.538	2.537	60
1 0 2	2.790	2.789	90	1 1 2	2.418	2.417	70	2 0 0	2.327	2.328	80
1 1 2	2.355	2.354	95	2 0 0	2.252	2.252	90	1 1 3	2.068	2.072	15
2 0 0	2.195	2.195	95	1 0 3	2.171	2.173	5	2 1 1	2.014	2.017	15
1 0 3	2.112	2.112	20	2 1 1	1.944	1.945	10	2 0 2	2.010	2.008	20
2 0 1	2.100	2.100	10	2 0 2	1.926	1.926	10	0 0 4	1.994	1.991	20
1 1 3	1.903	1.903	10	2 1 2	1.771	1.772	85	2 1 2	1.845	1.846	90
2 1 1	1.895	1.894	80	1 0 4	1.718	1.718	15	1 0 4	1.833	1.831	60
2 0 2	1.876	1.876	35	2 2 0	1.592	1.594	20	1 1 4	1.705	1.705	45
2 1 2	1.725	1.725	80	2 1 3	1.563	1.563	5	2 2 0	1.645	1.647	30
1 0 4	1.671	1.670	25	3 0 1	1.471	1.471	2	3 0 1	1.523	1.522	10
2 0 3	1.622	1.622	5	2 2 2	1.464	1.464	2	2 0 4	1.514	1.515	10
2 2 0	1.552	1.553	40	3 1 0	1.424	1.425	20	1 0 5	1.509	1.512	15

oxyhalides (*11*), the fluorochlorides can be described as an arrangement of linked cation coordination polyhedra of high coordination number, whereas the fluoroiodides must be visualized as a layer structure with a reduced number of nearest neighbors for the cations.

The fact that all fluorohalides of Eu(II) adopt the same structure as the Sr compounds with only slightly different lattice parameters is plausible but not necessarily to be expected. Due to this close similarity it is not surprising that the Eu^{2+} cations can be substituted easily for Sr^{2+}. By adding approximately 1 % EuF_2 in the preparation we obtained Sr(EU)F*X* compounds which fluoresce in uv light. The fluorescence colors of the pure EuF*X* compounds and those of the doped Sr(EU)F*X* compounds show a similar scale from a reddish to a bluish purple. However, to the naked eye it seems that particle size, impurities, and the concentration of the doping cation can affect the tinges of red or blue, but fluorescence spectra are not yet available.

Discussion

In discussing the crystal chemistry of rare earth oxyhalides (*Ln*OX) it has been emphasized (*11*, *15*) that the strong, partially covalent bonding between the cations and the oxygen dominates the geometry of the structure. In some cases, this leads to a considerable compression of the larger anions (*X*) with *X*–*X* distances falling short of the sum of the usually accepted ionic radii. This holds only to a smaller extent for the *M*H*X* and *M*F*X* compounds. The *M*–H and *M*–F bonds are also very short (*4*, *16*), but the larger anions are only slightly compressed in the hydridebromides, hydrideiodides, fluorobromides, and fluoroiodides of Ca, Sr, and Eu. The close interaction of the cations with the fluoride anions is clearly reflected in the findings of Cevey and Lacroix (*17*). In epr measurements of Mn^{2+} substituting Sr^{2+} in SrFCl, they have discovered a hyperfine structure due to an interaction with the four F^- neighbors, whereas the five almost equivalent Cl^- neighbors—in the mean only 0.6 Å farther away—show no such affect.

It is remarkable that all variations of these cations and anions differing so much in size and polarizability lead to the same structure type. The structural differences within this arrangement, ranging from a coordination lattice (*Ln*OCl, *M*FCl) to a layer structure (*Ln*OI, *M*FI), have been discussed in detail (*11*). The borderline of the range of existence is reached with the oxyhalides of the heavier rare earths, ErOCl being dimorphic and TmOCl, YbOCl, and LuOCl only crystallizing in a different arrangement. With respect to their instability and peritectic decomposition, the mixed halides of Ca represent a similar borderline even though polymorphism has not yet been observed. The fact that the calcium hydridehalides are well defined with congruent melting points can be explained with the greater softness and polarizability of the hydride ion as compared with the fluoride anion.

In a plot of *c*/*a* ratios versus cation parameters, Flahaut (*18*) showed that structures with the PbFCl arrangement are clearly

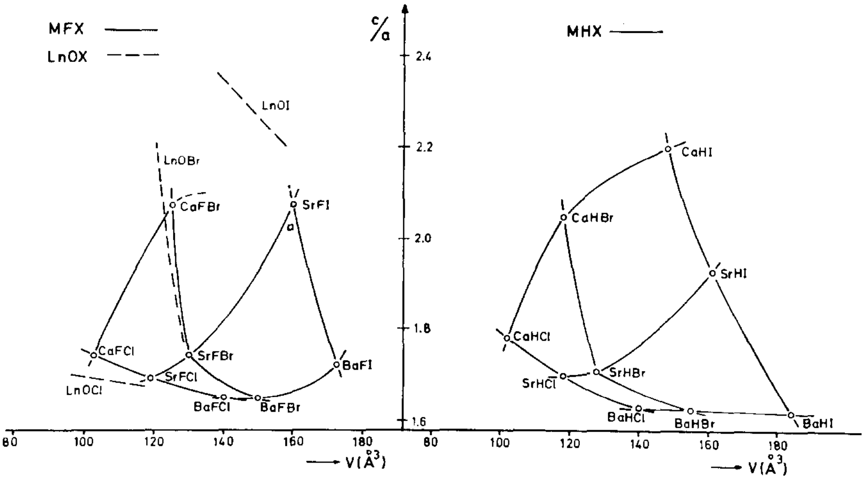

FIG. 1. Plots of *c*/*a* ratios vs cell volume for *M*F*X*, *M*H*X*, and *Ln*O*X* compounds.

separated from those of the anti-Fe_2As-type which crystallize with the same space group and quite similar lattice parameters. We want to emphasize that within its field of existence, the PbFCl-type structure itself shows marked differences with respect to crystal chemistry and structural geometry.

The close resemblance of the *MFX* and *MHX* systems is best demonstrated by the similarity of the plots of the *c*/*a* ratios versus cell volume (Fig. 1). In addition, the dashed lines give the curves for the rare earth oxyhalides exhibiting quite similar gradients within their range and showing that they cover only a section of the field within which this structure is found to be stable. It is only in the different behavior of the oxyiodides with their large *c*/*a* ratios that the effect of the higher electrostatic charges becomes evident. Here the *a* lattice parameter is comparatively contracted, leading to the compression of the larger anions mentioned above, and the necessary volume is arrived at by large *c* parameters. The similarity of the *MHX* and *MFX* diagrams is very instructive. It is evident that the point for the questionable CaFI phase, graphed as a small square, is completely inconsistent with the corresponding CaHI point, suggesting that the phase is not CaFI. It might be a representative of a $CaF_{1-x}I_{1+x}$ system, but analytical data are not yet available.

Electrostatic calculations

If only electrostatic interactions are taken into account, a maximum lattice energy cannot be found by variation of the two free positional parameters, *z*(*M*) and *z*(*X*), of the PbFCl-type structure. Like other layer structures, the PbFCl arrangement collapses in such a calculation. With the counteracting repulsive forces lacking *z*(*M*) decreases and *z*(*X*) increases leading to a continuous contraction of the F–*M*–*X* triple layer. Figure 2 gives the values of the Madelung part of lattice energy U_e within the observed range of *z* parameters.[3] Using constant positional parameters but varying the *c*/*a* ratios, a maximum in lattice energy can be found, but the optimum *c*/*a* ratio does not depend on the volume, and this would correspond to straight lines parallel to the abscissa in the plot of Fig. 1. Of course, U_e itself decreases with increasing volume due to greater distances between the opposite ionic charges. For geometrical reasons, it is evident that *z*(*M*) should increase with increasing radius of the cation, and larger anions *X* lead to higher *z*(*X*) values. Such parameter changes will affect the *c*/*a* ratios, as is shown in Fig. 3, which gives the values of the optimum *c*/*a* ratios in the field of the two positional parameters. The results of these

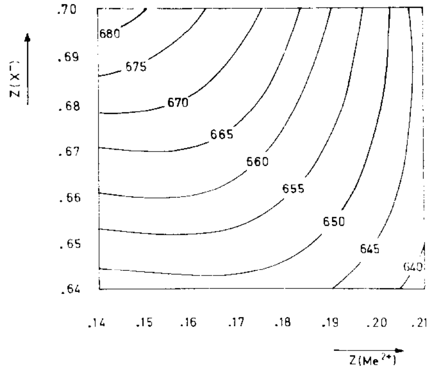

FIG. 2. Madelung part of lattice energy U_e within the usually observed range of positional parameters *z*(*M*) and *z*(*X*) for a cell volume of 100 Å^3 and a *c*/*a* ratio of 2.0. U_e values are given in kilocalories per mole.

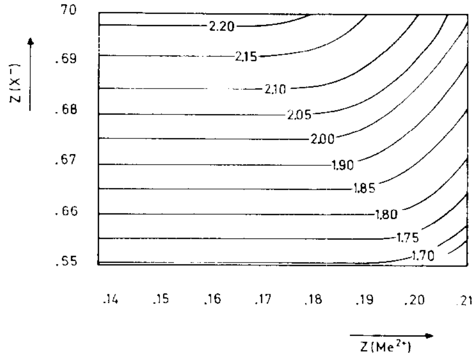

FIG. 3. Optimum *c*/*a* ratios with maximum U_e for varying positional parameters.

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[3] Electrostatic lattice energies were calculated with the program MANIOC, written by W. H. Baur, Chicago.

calculations can qualitatively explain the general outline of the diagram in Fig. 1.

Higher $z(X)$ values favor higher c/a ratios for electrostatic reasons and thus, in Fig. 1, the curves connecting compounds with the same cation but varying anions have a positive slope. The negative slope of the lines following compounds with different cations could be attributed in part to increasing $z(M)$ parameters; however, electrostatics alone contribute only little to this effect.

The detailed features of the diagram in Fig. 1 illustrate the importance of nonelectrostatic contributions in these ionic compounds. The great variations in electrostatics, ion size, and ion softness lead to very different cell geometries and structural variations within the "same" structure type.

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