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Simple Route to Lattice Energies in the Presence of Complex Ions

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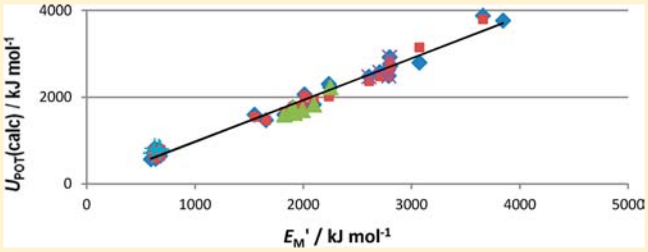

ABSTRACT: Lattice energies for ionic materials which separate into independent gaseous ions can be calculated by standard Born−Haber−Fajans thermochemical cycle procedures, based on the energies of formation of those ions. However, if complex ions (such as sulfates) occur in the material, then a sophisticated calculation procedure must be invoked which requires allocation of the total ion charge among the atom components of the complex ion and evaluation of the attractive and repulsive energy terms. If, instead, the total ion charge is allocated to the central atom of the complex ion (with zero charge on the coordinated atoms), to create a "condensed charge ion" (having zero self-energy), then a straightforward calculation of the electrostatic (Madelung) energy, E_M', correlates well with published lattice energies: U_{POT}/kJ mol^{-1} = $0.963E_M'$, with a correlation coefficient, $R^2 = 0.976$. E_M' is here termed the "condensed charge" electrostatic (Madelung) energy. Thus, using the condensed charge ion model, we observe that a roughly constant proportion (~96%) of the corresponding lattice energy arises from the electrostatic interaction terms. The above equation permits ready evaluation of lattice energies for ionic crystal structures containing complex ions, without the necessity to estimate any of the problematic nonelectrostatic interaction terms. A commentary by Prof. H. D. B. Jenkins substantiating this analysis is appended.

■ INTRODUCTION

Lattice (potential) energy, U_{POT}, is the sum of all the interactions, both attractive and repulsive, which occur between a formula unit and its (infinite) surroundings within a (usually crystalline) condensed material, including such interactions as Coulombic (charge), van der Waals, and even hydrogen bonding.[1] The Coulombic energy is also known as the Madelung energy, E_M (here used as positive, but often taken with a negative sign), and is rapidly calculated by standard computer programs.[2] In an ionic material with complex ions, U_{POT} is the energy required to separate the constituent ions to infinite separation in the gas phase—but it is not experimentally measurable and must be calculated. U_{POT} is useful in that it completes the thermochemical cycle relating to the formation of a condensed ionic material and is used in confirmation of the material's thermodynamic stability or otherwise. Lattice energy is little different from lattice enthalpy, $\Delta_L H$, and the two may readily be interconverted.[3]

There are two methods by which lattice energies may be obtained. If the formation energy, $\Delta_f U$ (or formation enthalpy, $\Delta_f H$), of the material is known, then a Born−Haber−Fajans thermochemical cycle (BHFC) may be invoked, using the known formation energies of the material and of the gaseous ions concerned, with the lattice energy closing the cycle.

Alternatively, the lattice energy may be calculated directly by summation of all the interactions within the known crystal structure. This is, of course, a fraught and difficult process since it requires knowledge of the individual ion charges and their locations in order to calculate the Madelung energy, as well as the modes and extents of other non-Coulombic interactions, attractive and repulsive, which may occur with the surrounds. These calculations may be performed by using empirical interaction formulas (such as the Buckingham potential),[4] which require many parameters to be supplied, or by ab initio quantum methods, with their own complex issues.

■ MADELUNG ENERGIES OF COMPLEX IONS

The principal contributor to ionic lattice energies is the electrostatic component. In a recent analysis,[5] we have shown that there is a strong correlation between lattice energy and electrostatic (Madelung) energy for the many ionic materials which decompose directly into monatomic gaseous ions, such as

$$\mathrm{NaCl(s)} \rightarrow \mathrm{Na^+(g)} + \mathrm{Cl^-(g)} \quad \text{or even}$$

$$\mathrm{Sr_2MoO_4(s)} \rightarrow \mathrm{2Sr^{2+}(g)} + \mathrm{Mo^{4+}(g)} + \mathrm{4O^{2-}(g)}$$

where U_{POT}/kJ mol^{-1} = $0.8519E_M + 293.9$, with a correlation coefficient, $R^2 = 0.995$. This result implies that the attractive electrostatic energy is reduced by up to ~15%, through repulsive interactions, to yield the lattice energy.

However, it is often both convenient and conventional to regard the more complex ionic materials as consisting of complex ions[6] rather than monatomic ions, such as

$$\mathrm{Sr_2MoO_4(s)} \rightarrow \mathrm{2Sr^{2+}(g)} + \mathrm{MoO_4{}^{4-}(g)} \qquad \text{or}$$

$$\mathrm{(NH_4)_2SO_4(s)} \rightarrow \mathrm{2NH_4{}^+(g)} + \mathrm{SO_4{}^{2-}(g)}$$

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In order to perform an electrostatic (Madelung) calculation with complex ions, it becomes necessary to estimate a distribution of the charges within the complex ion. To see if an appropriate distribution can be selected, we have calculated[2] the Madelung energies of K_2PtCl_6, with the crystal structure fixed, for Pt charges from +4 to −2 (the Cl^- charges are given by $q(\mathrm{Cl}) = [-2 - q(\mathrm{Pt})]/6$); the calculated Madelung energies are plotted in Figure 1.

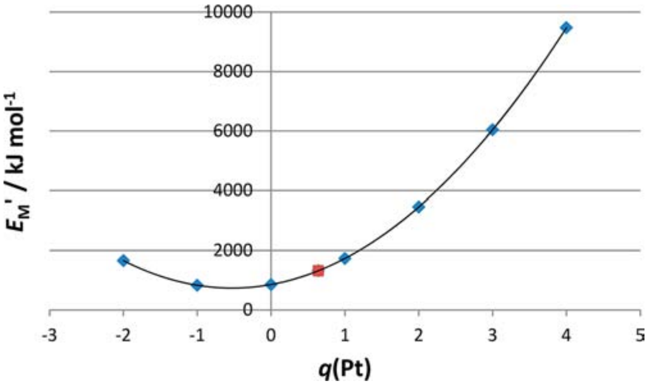

Figure 1. Madelung energies, E_M, plotted against putative Pt charges from +4 to −2 for K_2PtCl_6. The choice of $q(\mathrm{Pt}) = 0.64$ made by Jenkins and Pratt[7] is marked with a red square.

As can be seen from the figure, the Madelung energies decrease as the Pt charge decreases, corresponding to the reduction in the (internal) self-energy of the $PtCl_6^{2-}$ complex ion. The curve is quadratic (with the constant term arising from K^+-K^+ interactions, the term linear in q from K^+-q interactions, and the term squared in q from $q-q$ interactions), and there is no obvious "correct" choice of charge. Jenkins and Pratt,[7] in their analysis of the energetics of K_2PtCl_6, using the same crystal structure, chose a value of $q(\mathrm{Pt}) = 0.64$ relative to their assessment of all contributions to the lattice energy. Their electrostatic term thus includes a contribution from the self (internal) energy[8] of the $PtCl_6^{2-}$ ion.

Since the self-energy arises only from the internal charge interactions within the complex ion and does not contribute to the lattice energy, we have considered the alternative strategy of condensing the full charge of the complex ion onto the central atom (−2 on Pt in this case), with zero charge on the coordinated atoms (Cl in this case), while retaining the crystal structure unchanged. We term this the "condensed charge" ion, and it has no electrostatic self-energy. This strategy roughly corresponds to application of Gauss's law for a sphere with a uniform surface charge totalling q; namely, that the electric field outside the sphere is identical to that of a point charge q at the center of the sphere.[9] The analogy is imperfect because the charge in the complex ion is not uniformly distributed across the surface of a sphere.

Nevertheless, on adopting this "charge condensation" strategy (without altering the positions of any of the atoms involved) for a wide range of materials containing complex ions (see Table 1), we find a good relation between lattice energy, U_{POT}, and condensed Madelung energy, E_M', as shown in Figure 2, where $U_{POT}/\mathrm{kJ\ mol^{-1}} = (0.958 \pm 0.031)E_M' + (18 \pm 66)$, with $n = 26$, and with a correlation coefficient, $R^2 = 0.976$. If the intercept is constrained to zero (which is well within the statistical error range), then we find an average correlation of $U_{POT}/\mathrm{kJ\ mol^{-1}} = 0.963E_M'$ (see legend to Figure 2 for details).

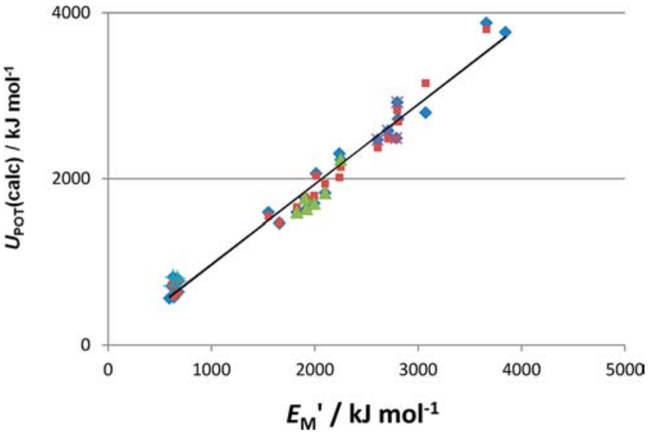

Figure 2. Calculated lattice energy, $U_{POT}(\mathrm{calc})$,[10] plotted against condensed charge Madelung energy, E_M', where the least-squares fit yields $U_{POT}/\mathrm{kJ\ mol^{-1}} = (0.958 \pm 0.031)E_M' + (18 \pm 66)$, with a correlation coefficient, $R^2 = 0.976$ (with intercept constrained to zero then $U_{POT}/\mathrm{kJ\ mol^{-1}} = 0.966E_M'$, $R^2 = 0.976$). Red squares represent $U_{POT}(\mathrm{BHFC})$[10] values, for comparison with the fit for the $U_{POT}(\mathrm{calc})$ values, and have not been included in the fitting calculation; but they have a very similar zero-intercept fit of $U_{POT}/\mathrm{kJ\ mol^{-1}} = 0.961E_M'$ with $R^2 = 0.976$. As a compromise, we will use the mean slope in our analyses: $U_{POT}/\mathrm{kJ\ mol^{-1}} = 0.963E_M'$. Blue diamonds are for $U_{POT}(\mathrm{calc})$ values;[10] overlaid crosses are for MSO_4; overlaid green triangles are for M_2SO_4; and overlaid pluses are for halates (see Table 1).

This relation suggests that the nonelectrostatic interactions reduce the lattice energy by about 3−4%. (In the case of a material formed of monatomic ions,[5] the electrostatic contribution is reduced by up to ∼15% by repulsive interactions.)

It should be appreciated that neither the reference[10] BHF cycle nor the calculated lattice energies are themselves definitive, each being subject to experimental and calculational uncertainties. The percentage differences between reference BHFC and calculated values of U_{POT} for the literature data in Table 1 range from +14% (for Na_2CO_3) to −11% (for $Zn(OH)_2$) but are generally below 5%. The complementary volume-based thermodynamic (VBT) estimation[11] of lattice energies (which, however, dispenses with crystal structure information) has somewhat larger mean deviations, ranging from +24% to −13%.

From the large deviations seen in the Table, it is clear that the reported U_{POT} values for the halates may be unreliable, and indeed, the chlorate values have already been superseded by resorting to VBT values.[14]

■ CONVERTING BETWEEN SIMPLE AND COMPLEX IONS

As discussed in the Introduction, it is possible to consider an ionic material as consisting either of monatomic ions or as a mixture of monatomic and complex ions. In order to illustrate this, we consider the case of K_2NaScF_6, an example of the ternary mineral type elpasolite.[15,16]

Marx has determined the enthalpy of formation from a Born−Haber−Fajans thermochemical cycle,[15] using the enthalpic properties of the individual ions, as −3397.6 kJ mol^{-1}, and has calculated a corresponding lattice energy of 8162.2 kJ mol^{-1}, using a Buckingham potential. However, it is of interest to also consider this material as a mixture of $2K^+$, Na^+, and

Table 1. Condensed Charge Madelung Energies, E_M', Calculated Lattice Energies, U_{POT}(calc), and Born−Haber−Fajans Thermochemical Cycle Lattice Energies, U_{POT}(BHFC), from Reference 10 for a Variety of Materials Having Complex Ions[a]

	kJ mol^{-1}			nm^3	kJ mol^{-1}	%	kJ mol^{-1}	%
		U_{POT}: HCP[10]						
	E_M'	(calc)	(BHFC)[b]	$V_m{}^c = V_{cell}/Z$	U_{POT}: E_M' estimate	% diff	U_{POT}: VBT estimate[d]	% diff
				MX (1:1)				
$CsMnO_4$	594	565		0.1169	572	−1.2	584	−3.3
$KMnO_4$	629	607		0.0963	606	0.2	616	−1.4
$RbBF_4$	637	577	590	0.0936	613	−6.3	620	−7.5
$NaClO_4$	679	643	641	0.0810	654	−1.7	646	−0.5
				various				
$Ba(NO_3)_2$	2012	2062	2035	0.1338	1938	6.0	1938	6.0
$Zn(OH)_2$	3073	2795	3151	0.0534	2959	−5.9	2501	10.5
$Mg_3(PO_4)_2/3$[e]	3660	3877	3802	0.0528	3525	9.1	3986	−2.8
Na_3VO_4	3845	3766		0.1186	3703	1.7	3731	0.9
				M_2X (1:2)				
Li_2SO_4	2251	2229	2142	0.0823	2167	2.8	2096	5.9
Na_2SO_4	2099	1827	1938	0.0868	2021	−10.6	2056	−12.5
K_2SO_4	1994	1700	1796	0.1074	1920	−13.0	1903	−11.9
Rb_2SO_4	1920	1636	1748	0.1217	1849	−13.0	1818	−11.1
Cs_2SO_4	1826	1596	1658	0.1418	1759	−10.2	1718	−7.7
$(NH_4)_2SO_4$[f]	1904	1766	1777	0.1240	1834	−3.8	1805	−2.2
Na_2CO_3	2237	2301	2016	0.0705	2155	6.4	2217	3.6
K_2PtCl_4	1551	1594	1550	0.2009	1494	6.3	1510	5.2
K_2PtCl_6	1657	1468	1471	0.2276	1596	−8.7	1442	1.8
				MX (2:2)				
$CaSO_4$	2790	2489	2480	0.0768	2687	−7.9	2720	−9.3
$SrSO_4$	2708	2577	2484	0.0769	2608	−1.2	2718	−5.5
$BaSO_4$	2608	2469	2374	0.0867	2511	−1.7	2631	−6.6
$MnSO_4$	2798	2920	2825	0.0724	2694	7.7	2764	5.3
$SrCO_3$	2806	2720	2688	0.0648	2702	0.7	2850	−4.8
				halates (1:1)				
$NaBrO_3$	669	803	791	0.0754	644	19.8	659	17.9
$NaClO_3$	682	770	785	0.0711	657	14.7	670	13.0
$KClO_3$	614	711	721	0.0922	591	16.8	623	12.4
KIO_3	629	820	780	0.0909	606	26.1	625	23.7

[a] The column labelled "U_{POT}: E_M' estimate" is the estimate of U_{POT} using the linear least-squares fit of Figure 2, with "% diff" relative to the U_{POT}(calc) value. Similarly, the column labelled "U_{POT}: VBT estimate" is the estimate of U_{POT} using the volume-based thermodynamic (VBT) procedure based on the formula volume in the column "V_m", with "% diff" relative to the U_{POT}(calc) value. [b] BHFC = Born−Haber−Fajans thermochemical cycle. [c] V_m is the formula volume, V_{cell} is the crystallographic unit cell volume, and Z is the number of formula units contained within the unit cell. Data are from refs 12 and 13. [d] VBT equation[11] for $U_{POT} \leq 5\,000$ kJ mol^{-1}: $U_{POT} = 2I[(\alpha/V_m{}^{1/3}) + \beta]$. [e] The data $Mg_3(PO_4)_2$ have been divided by 3 in order to avoid overweighting of the datum. [f] For $(NH_4)_2SO_4$, both the ammonium and the sulfate ions have been treated as condensed charge ions.

$ScF_6{}^{3-}$ ions. Figure 3 shows the two options in a thermochemical cycle diagram.

We can estimate the lattice energy, U_{POT}, of the complex ion, $ScF_6{}^{3-}$, (without resorting to an elaborate Buckingham potential) by calculating the condensed charge Madelung energy (which yields $E_M' = 3628$ kJ mol^{-1}) and then converting according to our here-established relation $U_{POT} = 0.963E_M' = 3494$ kJ mol^{-1}. By difference, the dissociation energy in the gas phase of the $ScF_6{}^{3-}$ anion is then 8162 − 3494 = 4668 kJ mol^{-1}. Now, with the above data and the formation enthalpies[10,15] of Sc^{3+} (4637.6 kJ mol^{-1}) and F^- (−248.8 kJ mol^{-1}), one may calculate the energy of formation of $ScF_6{}^{3-}$(g):

$$Sc(s) + 3F_2(g) \xrightarrow{4638-6\times 249} Sc^{3+}(g) + 6F^-(g) \xrightarrow{-4668} ScF_6{}^{3-}(g)$$

Thus,

$$\begin{aligned}\Delta_f U(ScF_6{}^{3-}, g)/\text{kJ mol}^{-1} &= 4638 - 6 \times 249 - 4668 \\ &= -1524\end{aligned}$$

and

$$\Delta_f H(ScF_6{}^{3-}, g)/\text{kJ mol}^{-1} = -1524 + RT = -1522$$

The large negative value for $\Delta_f H(ScF_6{}^{3-}, g)$ implies considerable covalency in this complex of scandium surrounded by six fluoride ions at the crystal distance, comparable with the value[17,18] for the hexafluorosilicate anion, $SiF_6{}^{2-}$, (−2161 kJ mol^{-1}) but contrasted with the much smaller value for, say, the hexachloropalladate anion, $PdCl_6{}^{2-}$, (749 kJ mol^{-1}).

The results of our calculations for K_2NaScF_6 are summarized in Table 2. It is seen that the E_M' estimate[5] for U_{POT} closely matches (within 1%) the value obtained by Marx.[15] On the other hand, the VBT estimate[11] of U_{POT} for the monatomic ion

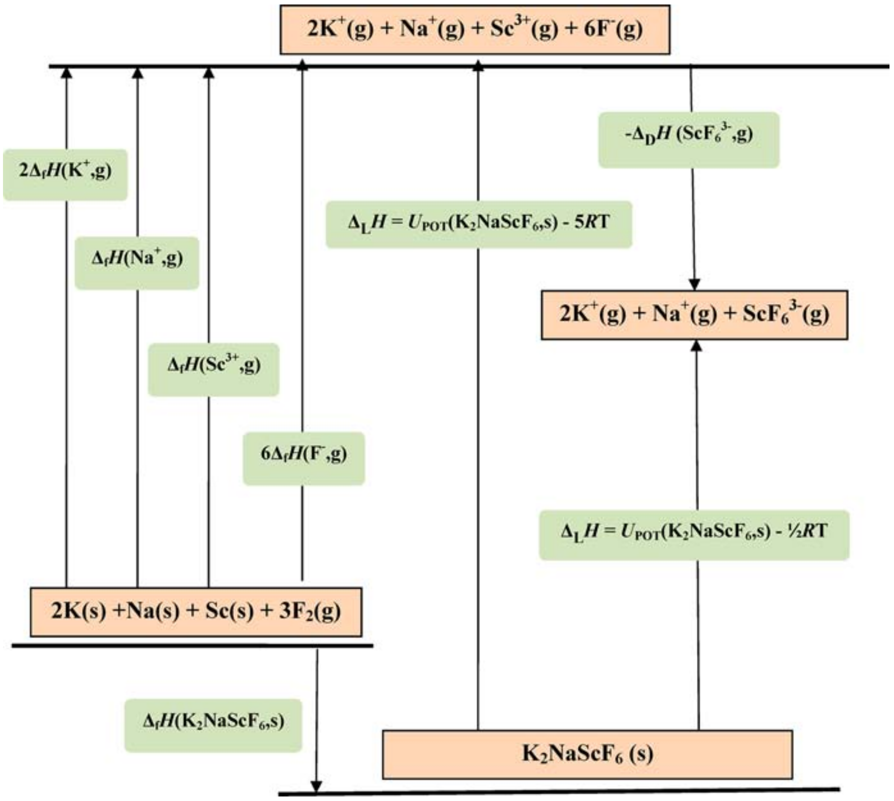

Figure 3. Thermochemical cycle diagram for the elpasolite K_2NaScF_6, considered either as a mixture of monatomic ions or as monatomic cations plus the polyatomic anion, ScF_6^{3-}. The quantity $\Delta_D H$ corresponds to the enthalpy of the gas phase dissociation of the ScF_6^{3-} ion. The conversion from lattice energy, U_{POT}, to lattice enthalpy, $\Delta_L H$, follows from the equation:[3] $\Delta_L H = U_{POT} + \sum_i s_i((c_i/2) - 2)RT$, where s_i = number of ions of type i, and c_i represents the degrees of freedom of the gaseous ion (3 for monatomic, 5 for linear polyatomic, and 6 for general polyatomic ions).

Table 2. Calculated Energies for K_2NaScF_6 Based upon Various Assumptions[a]

form of solid	Madelung energy	Born–Haber–Fajans cycle[15]	$V_m = V_{cell}/Z$	U_{POT}: E_M estimate	U_{POT}: VBT estimate[b]
monatomic ions	9148	8162	0.1520	8087	(5365)[c]
				E_M' estimate	
condensed charge complex ion	3628		0.1520	3494	3461
$\Delta_D U$ (ScF_6^{3-}, g)				4668	
$\Delta_f H$(ScF_6^{3-}, g)				−1522	

[a] Column headings are as listed for Table 1. $\Delta_D U(ScF_6^{3-}, g)$ is the dissociation energy of the ScF_6^{3-} ion in the gas phase. [b] VBT equation[11] for $U_{POT} \leq 5000$ kJ mol^{-1}: $U_{POT} = 2I((\alpha/V_m^{1/3}) + \beta)$. [c] VBT equation[11] for $U_{POT} > 5000$ kJ mol^{-1}: $U_{POT} = AI(2I/V_m)^{1/3}$ with $A = 121.4$ kJ mol^{-1} nm.

description deviates considerably from the Born–Haber–Fajans cycle value; it is suggested that this discrepancy arises from the considerable covalency noted above within the ScF_6^{3-} complex, contrary to the assumption of full ionicity in the VBT estimations—which are based upon oxidated species.[19] Conversely, the condensed charge ion energies in the final row of Table 2 are mutually consistent.

■ CONCLUSION

We have here developed a simple correlation for complex ions between the condensed charge Madelung energy, E_M', and the lattice energy, U_{POT}. This correlation permits ready calculation of lattice energy for materials containing complex ions, without resorting to sophisticated calculations.

The present method complements our earlier-established volume-based thermodynamic (VBT) method[11] and yields similar results. The VBT method does not require crystal structural information but does rely on strict iconicity.

■ COMMENTARY BY PROF. H. D. B. JENKINS (WARWICK), INCLUDED WITH PERMISSION

The present paper demonstrates that total lattice potential energy, U_{POT}, of a salt containing a complex ion can be computed much more readily if the charge in the complex ion is condensed to a single central point charge. This simplifies the original approach of Jenkins and Waddington,[20−23] made in the 1970s, by essentially removing the self-energy term.[20] In the original models, E_M equates to the Madelung energy, then labeled U_M, so that:

$$\begin{aligned} U_{POT}/E_M &= U_{POT}/U_M \\ &= [A_0 + (A_1 + B_1)q + (A_2 + B_2)q^2 - U_R \\ &\quad + U_D]/[A_0 + A_1 q + A_2 q^2] \end{aligned} \tag{1}$$

where U_R and U_D are the repulsive and dispersion energies, respectively, and A_i and B_i represent coefficients defined in the original papers.[20−23]

However, the present condensed charge model for the complex ion, with zero self-energy ($q = 0$), reduces this to

$$U_{\mathrm{POT}}/E_{\mathrm{M}}' = U_{\mathrm{POT}}/U_{\mathrm{M}} = [A_0 - U_{\mathrm{R}} + U_{\mathrm{D}}]/[A_0] \quad (2)$$

The results obtained for specific salts of azides,[21] nitrates,[22] and chromates[23] lead to $U_{\mathrm{POT}}/E_{\mathrm{M}}'$ ratios averaging 0.94, 0.93, and 0.9, respectively, close to the value 0.96 obtained here. In the chromate case, the dispersion term was approximated, and in the interim period, improved crystal structure data may have become available.

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Notes

The authors declare no competing financial interest.

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