

The Lattice Energies of the Cuprous Halides

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The Lattice Energies of the Cuprous Halides

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Following exactly the method employed in the case of the silver halides the lattice energies of the cuprous halides have been calculated. The exponential constant in the empirical repulsion equation expressing the positive repulsive potential between the ions is found to be almost the same as that for the silver halides. The energies of the

salts indicate that, particularly for the iodide there is not purely ionic binding. The lattice energies are calculated to be, for CuCl 216 kcal., CuBr, 208 kcal., CuI 199 kcal. The "experimental" values are, CuCl 221.9 kcal. CuBr 216.0 kcal. and CuI 213.4 kcal.

Introduction

R ECENTLY calculations have been made of the lattice energies of the alkali halides¹ and of the silver and thallous halides² following a method proposed by Born and Mayer.³ In this paper the arithmetical calculations are carried out for the cuprous halides.

The method is exactly the same as that used for the silver halides, and the Table I of this paper follows exactly the contents of Tables I, II, and III of the previous article.²

The compressibilities are taken from an article by Bridgman.⁴ The frequencies assumed for the negative ions are those assumed for the silver salts. The polarizability of the cuprous ion is taken from Pauling.⁵ The experimental lattice constants assumed are those of the *Strukturbericht*.⁶ The energies of reaction are all taken from *International Critical Tables*, with the exception of the heat of sublimation of copper, which is estimated from the boiling point with the aid of Hildebrand's modification of Trouton's rule. The electron affinity of the halides are taken from the calculations on the alkali halides.¹

The disagreement of 2.9, 5.0, and 11.4 kcal. for the chloride, bromide, and iodide, respectively,

between the theoretical lattice energies and the "experimental" values, may in part be due to an uncertainty in the heat of sublimation of copper; however, it is more probable that they

TABLE I.

1 Salt 2 Crystal type 2 CuCl Zincblend 2 Zincblend 3 Qw2 (neg. ion) ×10½ crgs/molecule 4 ϵ (neg. ion) ×10½ crgs/molecule 5 α (neg. ion) ×10½ crm³ 3.40 4.08 5.27 7.29 6 α (pos. ion) ×10½ crm³ 0.43 0.43 0.43 0.43 7 ϵ (pos. ion) ×10½ crgs/molecule 2 Q9 29 29 29 29 29 29 29 29 29 29 29 29 29	=				
2 Crystal type 3 Q ₀₀ ² (neg. ion) ×10 ¹⁶ cm ² 4 ε (neg. ion) ×10 ¹² ergs/molecule 5 α (neg. ion) ×10 ¹² ergs/molecule 5 α (neg. ion) ×10 ¹² cm ³ 0.43 0.43 0.43 7 ε (pos. ion) ×10 ¹² cm ³ 0.43 0.43 0.43 0.43 0.43 0.43 0.43 0.43	1	Salt	CuCl	CuBr	Cul
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5 α (negs. ion) ×10 ²⁴ cm³ 3.45 4.47 7.29 6 α (pos. ion) ×10 ¹² cm³ 0.43 0.43 7 ε (pos. ion) ×10 ¹² ergs/molecule 29 29 29 29 29 29 29 29 29 29 29 29 29					
6 α (pos. ion) ×10½ crgs/molecule 29 29 29 29 8 $c_{++} \times 10\%$ ergs × cm³ 0.41 0.41 0.41 0.41 9 $c_{} \times 10\%$ " 21.9 27.3 37.7 11 $d_{++} \times 10\%$ ergs × cm³ 0.2 0.2 0.2 0.2 12 $d_{} \times 10\%$ " 27.0 470 1230 37.7 12 $d_{} \times 10\%$ " 27.0 470 1230 13 $d_{+-} \times 10\%$ " 27.0 470 1230 13 $d_{+-} \times 10\%$ ergs × cm³ 0.2 0.762 0.	- 5	α (neg. ion) $\times 10^{24}$ cm ³			
7 e (pos. ion) ×10 ¹² ergs/molecule	6	α (pos. ion) $\times 10^{24}$ cm ³			
8 c ₊ × 10% ergs × cm ⁶					
9 c − × 10% " " 133 208 437 10 c + × 10% " " 21.9 27.3 37.7 11 d + + × 10% ergs × cm8 0.2 0.2 0.2 0.2 12 d − × 10% " 270 470 1230 13 d + × 10% " 27 38 64 4.354 4.354 4.354 4.354 5.6′ 0.762 0.762 0.762 16 Ss′ 0.762 0.762 0.762 17 Ss′′ 0.253 0.253 0.253 17 Ss′′ 0.253 0.253 0.253 18 C × 10% ergs × cm8 146 198 330 19 D × 10% ergs × cm8 146 198 330 19 D × 10% ergs × cm8 150 220 420 18 S × 10% Compressibility bars 1 2.51 2.93 2.81 22 V $^{-1}(9V/dT)_p \times 10^g$ 65.4 62.1 73.5 23 9V/Nβ × 10½ ergs/molecule 142 141 177.5 24 (3T/Nβ) ($\partial V/\partial T)_p \times 10^g$ 65.4 62.1 73.5 25 $\partial V/\partial B \times 10^{12}$ ergs/molecule 15.97 15.20 14.26 26 $C/r_0^8 \times 10^{12}$ ergs/molecule 0.94 0.88 1.32 27 $\partial V/\partial B \times 10^{12}$ ergs/molecule 0.94 0.89 1.01 27 $D/r_0^8 \times 10^{12}$ ergs/molecule 0.89 0.89 1.01 27 $D/r_0^8 \times 10^{12}$ ergs/molecule 0.16 0.16 0.19 27 $\partial V/\partial B \times 10^{12}$ ergs/molecule 0.223 20 $\partial V/\partial B \times 10^{12}$ ergs/molecule 0.23 23 $\partial V/\partial B \times 10^{12}$ ergs/molecule 0.223 25 $\partial V/\partial B \times 10^{12}$ ergs/molecule 0.223 262 30 $\partial V/\sigma \times 10^{12}$ ergs/molecule 0.223 30 $\partial V/\sigma \times 10^{12}$ ergs/molecule 0.223 30 $\partial V/\sigma \times 10^{12}$ ergs/molecule 0.223 30 $\partial V/\sigma \times 10^{12}$ ergs/molecule 2.05 1.88 1.72 34 $\partial V/\partial B \times 10^{12}$ ergs/molecule 2.05 1.88 1.72 35 $\partial V/\partial B \times 10^{12}$ " 21.67 20.97 20.51 36 $\partial V/\partial B \times 10^{12}$ " 22.67 20.235 0.205 37 $\partial V/\partial B \times 10^{12}$ " 21.67 20.97 20.51 38 $\partial V/\partial B \times 10^{12}$ " 22.67 20.235 20.205 37 $\partial V/\partial B \times 10^{12}$ " 22.67 20.235 20.205 38 $\partial V/\partial B \times 10^{12}$ " 22.67 2.35 39 $\partial V/\partial B \times 10^{12}$ " 22.7 2.8 30 $\partial V/\partial B \times 10^{12}$ " 22.8 2.9 3.0 30 $\partial V/\partial B \times 10^{12}$ " 12.9 1.8 1.2 1.1 1.0 1.1 1.7 6 31 $\partial V/\partial B \times 10^{12}$ " 1.2 1.2 1.2 1.3 1.3 69 31 $\partial V/\partial B \times 10^{12}$ " 1.3 1.3 1.5 1.2 1.3 1.3 1.3 1.3 1.3 1.3 1.3 1.3 1.3 1.3	8	$c_{++} \times 10^{60} \text{ ergs} \times \text{cm}^6$	0.41		
10 c ₊ → X 10 ⁸⁰ " " 21.9 27.3 37.7 1 d ₊ + X 10 ⁸⁰ ergs × cm ⁸ 0.2 0.2 0.2 0.2 12 d _− → X 10 ⁸⁰ " " 270 470 1230 13 d ₊ → X 10 ⁸⁰ " " 270 38 64 1.354 4.354 4.354 4.354 5.5 c ₀ 0.762 0.		$c_{} \times 10^{60}$ "	133		437
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			21.9	27.3	37.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	11	$d_{++} \times 10^{76} \text{ ergs} \times \text{cm}^8$	0.2	0.2	0.2
13 $d_+ \to 10^{10}$ 27 38 04 4.354 4.354 4.354 4.354 15 S ₈ " 0.762 0.762 0.762 16 S ₈ " 0.253 0.25		$d_{} \times 10^{76}$ "	270	470	1230
14 S ₆ ' 4.354 4.354 4.354 5.5 S ₇ '' 0.762 0	13	$a_{+-} \times 10^{10}$	27	38	64
15 S ₈ " 0.762 0.762 0.762 0.762 16 S ₈ " 4.104 4.104 4.104 17 S ₈ " 0.253 0.253 0.253 0.253 18 C × 10 ⁵⁰ ergs × cm ⁶ 146 198 330 0.253 0.2	14	S_6'	4.354	4.354	4.354
17 Ss" 0.253 0.253 0.253 0.253 0.253 18 C × 1060 ergs × cm ⁶ 146 198 330 19 D × 1076 ergs × cm ⁸ 150 220 420 220 19 × 1076 (compressibility) bars 1.50 2.34 2.46 2.62 18 × 106 (compressibility) bars 1.50 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.81 2.97 2.51 2.93 2.97 2.95 2.97 2.97 2.97 2.97 2.97 2.97 2.97 2.97	15	$S_6^{\prime\prime}$	0.762	0.762	0.762
18 $\stackrel{\circ}{\times} \times 10^{80} \text{ergs} \times \text{cm}^6$ 146 198 330 19 D × 10% ergs × cm³ 150 220 420 20 rs × 10% cm 2.34 2.46 2.62 1 β × 10% (compressibility) bars 1 2.51 2.93 2.81 2 V $^{-1}(0V/\partial T)_p \times 10^6$ 65.4 62.1 73.5 2.93 2.81 2 V $^{-1}(0V/\partial T)_p \times 10^6$ 65.4 62.1 73.5 2.93 2.81 2 V $^{-1}(0V/\partial T)_p \times 10^{12}$ ergs/molecule 142 141 177.5 2 (3T/Nβ) ($\partial V/\partial T)_p \times 10^{12}$ ergs/molecule 0.94 0.88 1.32 25 $\alpha e^2/r_0 \times 10^{12}$ ergs/molecule 0.89 0.89 1.01 27 D/ro* × 10½ ergs/molecule 0.89 0.89 1.01 27 D/ro* × 10½ " " 21.67 20.97 20.51 29 σ × 10½ " " 21.67 20.97 20.51 29 σ × 10½ " " 21.67 20.97 20.51 29 σ × 10½ " " 21.67 20.97 20.51 29 σ × 10½ " " 21.67 20.97 20.51 29 σ × 10½ " " 21.67 20.97 20.51 29 σ × 10½ " " 21.67 20.97 20.51 29 σ × 10½ " " 21.67 20.97 20.51 20.205 31 ρ × 10% cm (average value = 0.223) 0.227 0.235 0.205 32 ro/ρ calculated from average 10.51 11.07 11.76 33 B(r) × 10½ ergs/molecule 2.05 1.88 1.72 34 ½hν × 10½ " " 14.89 14.32 13.69 36 U (theoretical lattice energy) kcal. 216 208 199 30 40 kcal. 208 38 MXer. → Ms.s. + ½X2s.s. 291°K, ΔH kcal. 2.8 2.9 3.0 30 MXer. 0°K → MXer. 291°K, ΔH kcal. 28.8 26.7 25.5 44 6 15.8 39 ½x2s.s. → Xρ 291°K ΔH kcal. 28.8 26.7 25.5 44 Mer. 291°K → Mρ 0°K " " -1.1 -1.1 -1.1 -1.1 +1.1 +1.1 +1.1 +1.1	16	S_8'	4.104	4.104	4.104
19 $D \times 10^{26} \text{ ergs} \times \text{cm}^8$ 150 220 420 $r_0 \times 10^{26} \text{ cm}$ 2.34 2.46 2.62 21 $B \times 10^{6} \text{ (compressibility) bars}^{-1}$ 2.51 2.93 2.81 2.97 $P \times 10^{10} \text{ (compressibility) bars}^{-1}$ 2.51 2.93 2.81 2.93 9V/Nβ × 10 ¹² ergs/molecule 142 141 177.5 24 (37/Nβ) (∂V/∂T) _P × 10 ¹² ergs/molecule 0.94 0.88 1.32 2.5 $ac^2 l/r_0 \times 10^{12} \text{ ergs/molecule}$ 15.97 15.20 14.26 26 $C/r_0^8 \times 10^{12} \text{ ergs/molecule}$ 0.89 0.89 1.01 27 $D/r_0^8 \times 10^{12}$ " 0.16 0.16 0.16 0.19 2.8 $\tau \times 10^{12}$ " 21.67 20.97 20.51 29 $\sigma \times 10^{12}$ " 22.3 220 262 30 σ/τ 10.3 10.5 12.8 10				0.253	
20 $r_0 \times 10^8$ cm	18	$C \times 10^{60} \text{ ergs} \times \text{cm}^6$		198	330
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$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21	$\beta \times 10^{6}$ (compressibility) bars ⁻¹			
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ergs/molecule 0.94 0.88 1.32 $25 \frac{\alpha e^3/r_0 \times 10^{12} \text{ ergs/molecule}}{25 \frac{\alpha e^3/r_0 \times 10^{12} \text{ ergs/molecule}}{215.97} 15.20 14.26 26 C/r_0^3 \times 10^{12} \text{ ergs/molecule}} 0.89 0.89 0.89 1.01 27 D/r_0^3 \times 10^{12} " " 0.16 0.16 0.16 0.19 28 τ × 10^{12} " " 21.67 20.97 20.51 29 σ × 10^{12} " " 21.67 20.97 20.51 29 σ × 10^{12} " " 223 220 262 30 σ/τ 10.3 10.5 12.8 31 \rho \times 10^{6} \text{ cm} (average value =0.223) 0.227 0.235 0.205 32 r_0/\rho calculated from average 10.51 11.07 11.76 33 B(r) \times 10^{12} \text{ ergs/molecule} 2.05 1.88 1.72 34 \frac{1}{2}hr \times 10^{12} \text{ ergs/molecule} 2.08 0.06 0.05 35 U \times 10^{12} \text{ " } " " 14.89 14.32 13.69 36 U \text{ (theoretical lattice energy) kcal. 216 208 199 3.0 MX cr. 0°K → MX cr. 291°K, ΔH kcal. 2.8 2.9 3.0 MX cr. \frac{\lambda}{2}M \text{ kcal.} 2.8 2.9 3.0 30 \frac{1}{2}X_2 s.s. \times X_0 291°K \Delta H \text{ kcal.} 28.8 26.7 25.5 40 X_0 291°K \rightarrow X_0 0°K " -1.1 -1.1 -1.1 -1.1 +1.1 +1.1 -1.1 4M cr. 0°K \rightarrow M_0 0°K " -86.5 -81.5 -74.2 42 Mcr. 291°K \rightarrow M_0 0°K " -86.5 -81.5 -74.2 42 Mcr. 291°K \rightarrow M_0 + e -0°K " 177.0 177.0 177.0 44 M_0 0°K \rightarrow M_0 + e -0°K " 177.0 177.0 177.0 177.0 45 Sum MX cr. \rightarrow M_0 + h e -0°K " 177.0 177.0 177.0 177.0 45 Sum MX cr. \rightarrow M_0 + h e -0°K " 177.0 177.0 177.0 177.0 47 Assumed value b 77.4 105.3 189.5 0 Experimental r_0 \times 10^8 \text{ cm} 2.34 2.49 2.59 50 Experimental r_0 \times 10^8 \text{ cm} 2.34 2.49 2.59 50 Experimental r_0 \times 10^8 \text{ cm} 2.34 2.49 2.59$			142	141	177.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	24		0.04	0.00	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					
27 $D/r^8 \times 10^{12}$ " " 0.16 0.16 0.19 28 τ $\times 10^{12}$ " " 21.67 20.97 20.51 29 σ $\times 10^{12}$ " " 223 20 262 30 σ/τ 10.3 10.5 12.8 1 ρ $\times 10^8$ cm (average value = 0.223) 0.227 0.235 0.205 32 r_0/ρ calculated from average 10.51 11.07 11.76 33 $B(r) \times 10^{12}$ ergs/molecule 2.05 1.88 1.72 34 $\frac{1}{2}h_P \times 10^{12}$ " 0.08 0.06 0.05 35 $U \times 10^{12}$ " " 14.89 14.32 13.69 36 U (theoretical lattice energy) kcal. 216 208 199 37 $MXer$, $0^9 K \rightarrow MXer$. 291°K, ΔH kcal. 2.8 2.9 3.0 38 $MXer$, $\rightarrow Ms$, s , $+\frac{1}{2}X_2s$, s , 291°K, ΔH kcal. 32.5 24.6 15.8 39 $\frac{1}{2}X_2s$, $s \rightarrow X_0$ 291°K ΔH kcal. 28.8 26.7 25.5 40 X_0 291°K $\rightarrow X_0$ 0°K " " -1.1 -1.1 -1.1 -1.1 1.1 1.1 1.1 1.1 1.1	25	$\alpha e^2/r_0 \times 10^{12}$ ergs/molecule			
28 τ × 10 ¹² " " 21.67 20.97 20.51 29 σ × 10 ¹² " " 223 220 262 30 σ/τ 21.88 31 $ρ$ × 10 ⁸ cm (average value = 0.223) 0.227 0.235 0.205 27 $ρ/ρ$ calculated from average 10.51 11.07 11.76 33 $B(r)$ × 10 ¹² " " 0.08 0.06 0.05 535 U × 10 ¹² " " 0.08 0.06 0.05 35 U × 10 ¹² " " 14.89 14.32 13.69 36 U (theoretical lattice energy) kcal. 216 208 199 37 M X c r, $Φ$ ° K → M X c r, 2 01° K , $Δ$ H kcal. 32.5 24.6 15.8 M X c r, $Φ$ H kcal. 32.5 24.6 15.8 39 $\frac{1}{4}$ X ₂ s.s. X + $\frac{1}{2}$ X ₂ s.s. 291° X , X +	20	$C/r_0^6 \times 10^{12}$ ergs/molecule			
28 σ × 1012 · / · · · · · · · · · · · · · · · · ·					
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		7 X 1014 /			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		σ Χ10 /			
32 ro/ρ calculated from average 10.51 11.07 11.76 33 B/r) × 101² ergs/molecule 2.05 1.88 1.72 34 $\frac{1}{2}h\nu \times 101²$ ergs/molecule 2.05 1.88 1.72 34 $\frac{1}{2}h\nu \times 101²$ "/ 14.89 14.32 13.69 35 $U \times 101²$ "/ 14.89 14.32 13.69 36 U (theoretical lattice energy) kcal. 216 208 199 37 $MXer$. $0^{\circ}\text{K} \rightarrow MXer$. 291°K, ΔH kcal. 2.8 2.9 3.0 38 $MXer$. $\rightarrow Ms$. s . $+\frac{1}{2}X_2$ s. s . 291°K, ΔH kcal. 32.5 24.6 15.8 39 $\frac{1}{2}X_2$ s. s . $\rightarrow X_{\theta}$ 291°K ΔH kcal. 28.8 26.7 25.5 40 X_{ϕ} 291°K $\rightarrow X_{\theta}$ 0°K " 1.1 -1.1 -1.1 -1.1 -1.1 1 1.1 4 1.1 -1.1 1 1.1 4 1.1 1.1 1.1 1.1 1.1 1.1 1.1					
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35 $U \times 10^{12}$ " 14.89					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					
$\begin{array}{cccccccccccccccccccccccccccccccccccc$					
ΔH kcal. 2.8 2.9 3.0 38 MX_{cr} . $\to M_s$.s. $+\frac{1}{2}X_2$ s.s. 291°K, ΔH kcal. 32.5 24.6 15.8 39 $\frac{1}{2}X_2$ s.s. $\to X_Q$ 291°K $\to M_g$ kcal. 28.8 26.7 25.5 40 X_Q 291°K $\to X_Q$ 0°K " -1.1 -1.1 -1.1 -1.1 41 X_Q +e ⁻ $\to X_Q$ -0°K " -86.5 -81.5 -74.2 42 M_c . 291°K $\to M_c$ -0°K " " -1.7 -1.7 -1.7 -1.7 43 M_c r. 0°K $\to M_Q$ -0°K " " 70.0 70.0 70.0 44 M_Q -0°K $\to M_Q$ -0°K " " 177.0 177.0 177.0 45 Sum MX_{cr} . $\to M_Q$ -+ X_Q -0°K (attice energy) ΔH kcal. 221.9 216.0 213.4 46 Difference 36 and 45 δΔH kcal. 2.9 5.0 11.4 74 Assumed value b. 27.4 105.3 189.5 48 " " b., 202 202 202 49 Calculated ro ×10° cm 2.34 2.49 2.59 50 Experimental ro × 10° cm 2.34 2.49 2.59			1. 210	200	177
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5,		2.8	2.0	3.0
$\frac{\Delta H}{\Lambda}$ kcal. 32.5 24.6 15.8 39 $\frac{1}{2}X_{2.s.8} \rightarrow X_0$ 291°K ΔH kcal. 28.8 26.7 25.5 40 X_0 291°K $\rightarrow X_0$ 0°K " -1.1 -1.1 -1.1 41 X_0 + $e^ \rightarrow X_0$ 0°K " -86.5 -81.5 -74.2 42 M_{Cr} .291°K $\rightarrow M_{Cr}$.0°K " " -1.7 -1.7 -1.7 -1.7 -1.7 -1.7 43 M_{Cr} .0°K $\rightarrow M_0$ 0°K " " 70.0 70.0 70.0 70.0 44 M_0 0°K $\rightarrow M_0$ 0°K $\rightarrow M_0$ 0°K " 177.0 177.0 177.0 45 Sum MX_{Cr} . $\rightarrow M_0$ + + e^- 0°K " 177.0 177.0 177.4 5 Unit central ΔH kcal. 22.9 216.0 213.4 46 Difference 36 and 45 δΔH kcal. 2.9 5.0 11.4 74 Assumed value b . 77.4 105.3 189.5 48 " b. b 202 202 202 49 Calculated t 0×10°s cm 2.34 2.49 2.59 50 Experimental t 0×10°s cm 2.34 2.49 2.59	38		2.0	4.7	0.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.0	ΔH kcal.	32.5	24.6	15.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	39				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	40	$X_a 291^{\circ} K \rightarrow X_a 0^{\circ} K$ " "			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	41	$X_a + e^- \longrightarrow X_a - 0$ °K " "	-86.5		-74.2
43 44 46 $^{$	42	M_{cr} , 291°K $\rightarrow M_{cr}$, 0°K " "	-1.7	-1.7	— 1.7
45 Sum MX_{cr} → M_g + X_g − 0°K (lattice energy) ΔH kcal. 221.9 216.0 213.4 46 Difference 36 and 45 $\delta \Delta H$ kcal. 2.9 5.0 11.4 47 Assumed value b 77.4 105.3 189.5 48 " 10.4 10.5 202 202 202 49 Calculated $r_0 \times 10^8$ cm 2.34 2.49 2.59 50 Experimental $r_0 \times 10^8$ cm 2.34 2.46 2.62	43	$M_{cr.}$ 0°K $\rightarrow M_{g}$ 0°K " "	70.0	70.0	70.0
45 Sum MX_{cr} → M_g + X_g − 0°K (lattice energy) ΔH kcal. 221.9 216.0 213.4 46 Difference 36 and 45 $\delta \Delta H$ kcal. 2.9 5.0 11.4 47 Assumed value b 77.4 105.3 189.5 48 " 10.4 10.5 202 202 202 49 Calculated $r_0 \times 10^8$ cm 2.34 2.49 2.59 50 Experimental $r_0 \times 10^8$ cm 2.34 2.46 2.62	44	$M_0 0^{\circ} \text{K} \rightarrow M_0^{+} + e^{-} 0^{\circ} \text{K}$ "	177.0	177.0	177.0
46 Difference 36 and 45 δΔH kcal. 2.9 5.0 11.4 47 Assumed value b 77.4 105.3 189.5 48 202 202 202 49 Calculated $to \times 10^6$ cm 2.34 2.49 2.59 50 Experimental $to \times 10^8$ cm 2.34 2.46 2.62	45	Sum $MX_{cr} \rightarrow M_{g}^{+} + X_{g}^{-} 0^{\circ} K$			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		(lattice energy) ΔH kcal.			
$\begin{array}{ccccccc} 48 & `` & b_{+} & 202 & 202 & 202 \\ 49 & \text{Calculated } r_0 \times 10^8 & \text{cm} & 2.34 & 2.49 & 2.59 \\ 50 & \text{Experimental } r_0 \times 10^8 & \text{cm} & 2.34 & 2.46 & 2.62 \\ \end{array}$					
48 0+ 202 202 202 49 Calculated r ₀ ×10 ⁸ cm 2.34 2.49 2.59 50 Experimental r ₀ ×10 ⁸ cm 2.34 2.46 2.62					
50 Experimental $r_0 \times 10^8$ cm 2.34 2.46 2.62		0+			
51 Difference $\delta r \times 10^8$ cm +0.002 -0.03 +0.03					
	51	Difference $\delta r \times 10^8$ cm	+0.002	-0.03	+0.03

¹ J. E. Mayer and L. Helmholz, Zeits. f. Physik 75, 16 (1932).

² J. E. Mayer, J. Chem. Phys. 1, 327 (1933).

³ M. Born and J. E. Mayer, Zeits. f. Physik 75, 1 (1932).

⁴ P. W. Bridgman, Proc. Am. Acad. Arts and Sci. 67, 345 (1932).

⁶ L. Pauling, Proc. Roy. Soc. (London) A114, 181 (1927). ⁶ P. P. Ewald and C. Hermann, Strukturbericht, 1913–1928.

show a considerable homopolar binding component. The calculated lattice constants (row 49) show irregular disagreement with the experimental values. This may in part be due to uncertainty in the experimental values but again is probably caused by an error in the assumptions. Table II, however, shows that the purely ionic crystal should be stable in crystal type in which these salts do crystallize, the Zincblend lattice.

Reliable evidence as to whether these crystals are in reality considerably homopolar or very nearly purely ionic can probably only be obtained

Table II. Calculation of the potential energy change with lattice type.

energies in 10⁻¹² ergs/molecule

	Experi-	••	Change at constant r_0 of					
Salt	mentally stable lattice	Hypo- thetical lattice	$-\frac{\alpha_e^2}{r_0}$	$-\frac{C}{r_0^6}$	$-\frac{D}{r_0^8}$	B(r ₀)	$\frac{\partial^2 \Phi}{\partial r^2} \frac{(\delta r)^2}{2}$	$\delta\Phi$
CuCl CuBr CuI	Zincblend Zincblend Zincblend	Rocksalt Rocksalt Rocksalt	-1.07 -1.02 -0.95	-0.73 -0.76 -0.95	-0.14			$+0.2 \\ +0.3 \\ +0.1$

by a theoretical calculation of the ionic nonelectrostatic (Heitler-London) repulsion from ionic electron wave functions.