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The Lattice Energies and Transition Temperatures of Caesium Chloride and Ammonium Chloride*

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The lattice energies of CsCl and NH_4Cl are calculated for both the CsCl type and NaCl type lattices, and the temperatures of transition between these two crystal forms determined from the equality of the free energies. This requires the computation of the elastic constants and proper frequencies. In determining the lattice energies, use is made of the method of Born and Mayer, four constants in the lattice energy expression being evaluated from experimental data. To obtain results consistent with known lattice constants, compressibilities and heats of transition, it is found necessary to multiply the van der Waals constants derived by Mayer by about 3.5 and to make the constant coefficient in the repulsion term for nearest like ions about 0.6 that for nearest (unlike) ions. Some success is attained in computing transition temperatures comparable with those known from experiment, but the temperature dependence found for the proper frequencies appears to be faulty.

INTRODUCTION

EXPERIMENT shows that at normal temperatures CsCl and NH_4Cl are stable in the CsCl type lattice, which is body-centered, and at higher temperatures in a simple lattice of the NaCl type. The transition temperatures are 184.3°C for NH_4Cl,[1] and about 445°C for CsCl.[2]

According to thermodynamics the form with the lowest free energy is stable. At low temperatures the free energy is practically equal to the total energy or to the negative lattice energy, $-U$, plus the zero point energy of the vibrations, so that at such temperatures the stable form is that which has the highest lattice energy. The stability of another form at higher temperatures requires that it have the lower free energy at those temperatures or, essentially that it have a higher entropy.

The free energy calculations require a knowledge only of the difference of lattice energies in the two forms and of the proper frequencies (acoustic and optical) of the lattices. To determine the difference of lattice energies, the shape of the potential energy curve must be known. The calculation of the frequencies requires also the computation of the elastic constants.

The lattice energy of the normally stable body-centered type has been calculated for NH_4Cl by Bleick[3] and for CsCl by Huggins and Mayer.[4] Born and Mayer,[5] Wasastjerna[6] and Jensen[7] have compared the lattice energies of the body-centered and simple lattice types of CsCl and have thus investigated the stability. Since none of these comparisons has resulted in the proper stability, the lattice energies have been recalculated. Apparently no previous attempt has been made to determine theoretically the temperature of transition.

LATTICE ENERGIES

In calculating the lattice energy, U, as a function of the lattice constant, r_0, that is, the smallest distance between ions in the lattice, Huggins and Mayer[4] and Bleick[3] have used the form

$$-U+\tfrac{1}{2}h\nu_0=\Phi(r_0)=-\alpha e^2/r_0-C/r_0^6 -D/r_0^8+B(r_0)+\tfrac{1}{2}h\nu_0. \quad (1)$$

The five terms included are, respectively: the electrostatic energy, the energies of the dipole-

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[1] P. W. Bridgman, Am. Acad. Proc. **52**, 91 (1916); F. E. C. Scheffer, Proc. Roy. Acad. Sci. Amsterdam **18**, 446 (1915).

[2] G. Wagner and L. Lippert, Zeits. f. physik. Chemie **31B**, 263 (1936); S. Zemczuzny and F. Rambach, Zeits. f. anorg. allgem. Chemie **65**, 403 (1910).

[3] W. E. Bleick, J. Chem. Phys. **2**, 160 (1934).

[4] M. L. Huggins and J. E. Mayer, J. Chem. Phys. **1**, 643 (1933).

[5] M. Born and J. E. Mayer, Zeits. f. Physik **75**, 1 (1932).

[6] J. A. Wasastjerna, Soc. Scient.-Fennica, Comm. Phys.-Math. vol. 8 No. 21 (1935).

[7] H. Jensen, Zeits. f. Physik **101**, 164 (1936).

TABLE I. *Constants which depend only on the lattice type.*

	TYPE OF LATTICE	
	CsCl	NaCl
α	1.7627	1.7476
S_6'	8.7088	6.5952
S_6''	3.5445	1.8067
S_8'	8.2077	6.1457
S_8''	2.1476	0.8001
M	8	6
M'	6	12
a	1.1547	1.4142
Δ	$(2r_0/\sqrt{3})^3$	$2r_0^3$

dipole and dipole-quadrupole van der Waals interactions, the repulsion component and the zero point energy of the vibrations. e is the electronic charge. The values of Madelung's constant, α, for the two lattice types involved are given in Table I.

The van der Waals constants C and D are of the forms[8]

$$C = S_6'c_{+-} + S_6''(c_{++} + c_{--})/2;$$
$$D = S_8'd_{+-} + S_8''(d_{++} + d_{--})/2$$

where the S's are numbers depending on the type of lattice and the c's and d's are constants characteristic for the interaction of a pair of ions. Table I lists the values of S obtained from the summations of Jones and Ingham.[9]

While the van der Waals terms constitute only a small part of the total energy, they change rapidly with variation of the lattice separation and are important for considerations of stability.

In this paper the constants c and d are, at first, given the values derived by Mayer[8] for CsCl from optical data, and by Bleick[3] for NH_4Cl. They are listed in Table II. The values of c obtained by Mayer for CsCl are considerably higher than those previously given by Mayer and Helmholz.[10]

It is assumed that the repulsion energy between two ions has the form $be^{-r/\rho}$ as given by Born and Mayer.[5] Because of the rapid decrease of the exponential form with increase of separation, it is necessary to include only the repulsion between a given ion and those ions nearest to it (unlike ions) and those at the next smallest distance (like ions). These we shall call first and second neighbors of that ion. The complete form assumed for the repulsion component, $B(r_0)$, will be considered in detail later.

The constants b and ρ can be evaluated if the compressibility, β, and lattice constant, r_0, are known, by forming the first and second derivatives of Eq. (1) with respect to r_0,

$$r_0\frac{\partial\Phi}{\partial r_0} = \frac{\alpha e^2}{r_0} + \frac{6C}{r_0^6} + \frac{8D}{r_0^8} + r_0\frac{\partial B}{\partial r_0} = R, \tag{2}$$

$$-r_0^2\frac{\partial^2\Phi}{\partial r_0^2} = \frac{2\alpha e^2}{r_0} + \frac{42C}{r_0^6} + \frac{72D}{r_0^8} - r_0^2\frac{\partial^2 B}{\partial r_0^2} = -S, \tag{3}$$

where, at absolute zero, $R=0$ and $S=9V/N\beta$. Since r_0 and β are not known at absolute zero, Born and Mayer derived the expressions

$$R = \frac{3T}{N\beta}\left(\frac{\partial V}{\partial T}\right)_P, \tag{2'}$$

$$S = \frac{9V}{N\beta}\left[1 + \frac{T}{\beta}\left(\frac{\partial\beta}{\partial T}\right)_P + \frac{T}{\beta^2 V}\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial\beta}{\partial P}\right)_T + \frac{2}{3}\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]. \tag{3'}$$

V is the mole volume; N, Avogadro's number; and P the pressure. With these expressions, the values at temperature T are used for all quantities occurring in (2) and (3). The calculations reported in this paper, except where otherwise noted, were made for 273°K.

At the temperatures involved, the classical value has practically been reached by the specific heats and therefore the heat energies have absorbed the zero point energies and become equal for the two lattice types. Since we shall be concerned primarily only with the difference of the energies in the two forms, the heat energy, and consequently the zero point energy, has been dropped.

The compressibility data for NH_4Cl were calculated from information supplied by Professor P. W. Bridgman to supplement that published[11] and the volume-temperature coefficient for CsCl was computed from the measurements of Wagner and Lippert.[12] All other quantities occurring in (2') and (3') have been taken from Huggins and

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[8] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933).

[9] E. Jones (Lennard-Jones) and A. E. Ingham, Proc. Roy. Soc. **A107**, 636 (1925).

[10] J. E. Mayer and L. Helmholz, Zeits. f. Physik **75**, 19 (1932).

[11] P. W. Bridgman, Phys. Rev. **38**, 182 (1931).

[12] Wagner and Lippert, reference 2.

Mayer and from Bleick. These data are listed in Table II.

The lattice constants of the body-centered and simple lattice types have been measured for both CsCl[12] and NH$_4$Cl,[13] but not at 273°. For the body-centered type we have only to correct for the change between room temperatures and 273°, but values for the simple lattices are available only at high temperatures and the thermal expansion coefficients are not known. The values given in Table II are approximations obtained by extrapolating from the measured data by means of the expansion coefficients of the body-centered type.

We shall write

$$B(r_0)=b_1Me^{-r_0/\rho}+b_2M'e^{-ar_0/\rho}, \tag{4}$$

so that

$$r_0\partial B/\partial r_0=-(r_0/\rho)(b_1Me^{-r_0/\rho}+b_2aM'e^{-ar_0/\rho}) \tag{5}$$

and

$$r_0^2\partial^2B/\partial r_0^2=(r_0^2/\rho^2)(b_1Me^{-r_0/\rho}+b_2a^2M'e^{-ar_0/\rho}). \tag{6}$$

The two terms represent the interactions with first and second neighbors and b_1 and b_2 are the corresponding values of b. M and M' are the numbers of first and second neighbors of an ion, and a is the ratio of the distances of second and first neighbors. Values of M, M' and a, which depend only on the type of lattice, are given in Table I.

It is to be expected that b will vary with the ions involved, so that it has been customary to introduce the two constants b_+ and b_-, one for each type of ion, and in place of b, to write b_+b_-, b_+b_+, or b_-b_- for interactions between two unlike ions, two positive ions or two negative ions, respectively. Then $b_1=b_+b_-$ and $b_2=(b_+b_++b_-b_-)/2$. Since there are now three unknowns, b_+, b_- and ρ, their evaluation requires the use of a third known quantity, in addition to the compressibility and lattice constant of the body-centered type at 273°. Born and Mayer[5] have used the experimentally determined "ionic radii" of Goldschmidt,[14] and Huggins and Mayer[4] and Bleick[3] have assumed ρ to have the average value, 0.345×10^{-8} cm, found for the alkali halides by Born and Mayer. For CsCl and NH$_4$Cl, Huggins and Mayer[4] and Bleick[3] have found b_+ and b_- to be only slightly different and the use of a single value of b appears entirely justified. Hence we shall, at first, assume that $b_1=b_2$.

b and ρ were determined for both salts from the compressibilities and lattice constants with Eqs. (2) and (3) for the body-centered type. Higher lattice energies were found for the NaCl type than for the CsCl type lattice for both salts and the former type should therefore be stable. This is contrary to experience. The values obtained are given in Table II under the heading "Original Data."

The conviction expressed by Mayer[8] that the van der Waals constants used provide stability for the body-centered form of CsCl is not confirmed. Born and Mayer,[5] starting with the smaller van der Waals constants already mentioned,[10] obtained the proper stability by an arbitrary doubling of the van der Waals energy but neglected the large effect of this change on the repulsion constants.

The fact that expression (1) fails to give the proper differences of lattice energies, may be due to the incorrect form of some of the terms as functions of r_0, to an inaccurate determination of the constants or to the omission of important components. The error is, of course, greatly magnified by taking small differences between large quantities.

The repulsion term should certainly be of more complicated form than that used. Wasastjerna[6] has attempted to arrive at a suitable form empirically, but has not obtained stability of the proper lattice type for CsCl. This he ascribes not to the incorrectness of the form used for the repulsion energy of individual ions, but to failure of additivity of the contributions of these pairs to the repulsion, when many ions are accumulated in a lattice. This would indicate the need, with the expression for the repulsion which he uses, for an additional term having a strong dependence on the lattice type, or for an equivalent modification of the form employed for the repulsion energy.

Jensen[7] has determined the lattice energies quantum mechanically, the repulsion being cal-

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[13] G. Bartlett and I. Langmuir, J. Am. Chem. Soc. **43**, 84 (1921).

[14] V. M. Goldschmidt, Skrifter Norske Videnskaps Akad. Oslo, No. 2 (1926), No. 8 (1927); Fortschr. d. Min. **15**, 73 (1931).

culated, without an empirical evaluation of constants, by Fermi statistics. He also found the simple lattice type stable for CsCl.

Since the method described, employing only two unknowns, b and ρ, failed to yield the proper stability, an attempt was next made to improve the results by increasing the number of constants that could be varied.

As mentioned before, the difference of lattice energies may, with sufficient accuracy, be assumed equal to the heat of transition at the equilibrium temperature. Experimentally determined values of the heats of transition for CsCl and NH_4Cl are given in the *International Critical Tables* and these are listed as "$\Delta\Phi$ kcal./mole (meas.)" in Table II.

This was now used to permit the evaluation of a third constant, a numerical factor inserted in both parts of the van der Waals energy and, of course, the same for both lattice types. It was found that the factors required to give the proper heat of transition for CsCl and NH_4Cl are 7 and 8.5, respectively. It is improbable that the van der Waals energies can be as large as these factors indicate.

More reasonable results are secured by changing the magnitude of the van der Waals terms and also admitting different coefficients in the repulsion terms of the first and second neighbors (that is, $b_1 \neq b_2$) without changing the form of any term. In order to determine the four constants now available, an additional relation was obtained by using the lattice constant of the NaCl lattice type at absolute zero in Eq. (2). A linear extrapolation from the known values of the lattice constant of the NaCl type lattice at high temperatures by means of the expansion coefficient of the body-centered type, gives 3.372×10^{-8} cm for CsCl and 3.184×10^{-8} cm for NH_4Cl and it was assumed that the correct values might be slightly higher than these.

It was found necessary to multiply the quantities c and d given in Table II, under the heading "Original Data," by factors of 3.6 and 3.5 for CsCl and NH_4Cl, respectively, and to assign values of 0.70 and 0.55 to the ratio b_2/b_1, the fraction by which the coefficient in the repulsion term for the first neighbors must be multiplied to obtain the coefficient for the second neighbors. The results for the two salts are rather similar, but the van der Waals factors are unsatisfactorily large. The complete results are given in Table II under the heading of "Adjusted" data.

By quantum mechanical methods, Neugebauer and Gombas[15] found the principal part of the polarization energy and the first van der Waals component for CaCl to be almost identical in magnitude as well as form. In the method we have used, such a polarization energy would be indistinguishable from the van der Waals energy and the value derived for C would be twice its true value. It is quite possible that for CsCl and NH_4Cl the polarization energy may be large enough to explain completely the large values found for C and D.

Wasastjerna[16] has neglected the repulsion contribution of the second neighbors as inconsiderable based on the empirical expression which he derived for the repulsion energy. If, in the process described using four unknowns, we drop the repulsion of the second neighbors, i.e., set $b_2 = 0$, we can, of course, still obtain the proper heat of transition, but for both salts, the equilibrium lattice constant of the simple lattice type at absolute zero is found to be unreasonably large, requiring a thermal expansion coefficient for the simple lattice type less than half that for the body-centered type. The experimentally determined values of the lattice constants in the vicinity of the transition point indicate that the two expansion coefficients do not differ greatly.

In this determination of four unknowns, the values were not obtained by exact solution, but were found after numerous trials to give suitable agreement. The procedure followed was to choose values of the factor inserted in the van der Waals terms and of the ratio of the repulsion coefficients in the terms of the second and first neighbors, i.e., b_2/b_1, and then by substitution to ascertain whether suitable values were obtained for the difference of lattice energies, ΔU, in the two crystal types and for the lattice constant of the simple lattice type at absolute zero.

In addition to the methods already described, an investigation was made for CsCl to see what results would be obtained by taking as the four

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[15] Th. Neugebauer and P. Gombas, Zeits. f. Physik **89** 480 (1924).

[16] J. A. Wasastjerna, Soc. Scient.-Fennica. Comm. Phys.-Math. vol. 8, No. 9 (1935).

constants, two values of ρ, ρ_1 and ρ_2 for the first and second neighbors, together with the van der Waals factor and a single value of b.

The form used for $B(r_0)$ was essentially that of Born and Mayer,[5]

$$B(r_0)=b\times 10^{-12}[Mb_+b_-e^{-r_0/\rho_1} \\ +\tfrac{1}{2}(1.25b_+^2+0.75b_-^2)e^{-ar_0/\rho_2}],$$

b_+ and b_- having the values found by Huggins and Mayer.[4] The results obtained were $b=1.73$, $\rho_1=0.364\times 10^{-8}$ cm, $\rho_2=0.310\times 10^{-8}$ cm and the van der Waals factor $=3.2$.

Subsequent calculations based on this method were found to differ little from those of the previous method of four constants, being slightly less satisfactory.

ELASTIC CONSTANTS AND ACOUSTIC FREQUENCIES

The elastic constants c_{11}, c_{12} and c_{44} were computed by the method of Born[17] from the expressions:

$$c_{11}=\frac{1}{\Delta}\sum\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi}{dr}\right)x^4+\frac{1}{2}\frac{dU}{d\Delta},$$

$$c_{12}=\frac{1}{\Delta}\sum\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi}{dr}\right)x^2y^2,$$

$$c_{44}=\frac{1}{2}\frac{dU}{d\Delta}+c_{12},$$

where $\frac{1}{2}\frac{dU}{d\Delta}=\frac{1}{6\Delta}r_0\frac{dU}{dr_0}=\frac{R}{6\Delta}$,

Δ is the volume per molecule and ϕ the mutual energy of a pair of ions. The summations are made by assuming a "reference" ion and summing over all other ions in the lattice. The electrostatic part of c_{11} is

$$(c_{11})_c=\frac{3e^2}{\Delta}\sum_{l_1l_2l_3}\frac{x^4}{r^5}(-1)^{l_1+l_2+l_3}. \tag{7}$$

The indices l_1, l_2 and l_3 are defined by the equa-

TABLE II. *Calculations are for $T=273$°K unless otherwise specified.*

SUBSTANCE	CsCl				NH$_4$Cl			
	Orig. Data		Adjusted		Orig. Data		Adjusted	
CRYSTAL TYPE	CsCl	NaCl	CsCl	NaCl	CsCl	NaCl	CsCl	NaCl
c_{++}	152	152			98	98		
c_{--} } $\times 10^{60}$ erg cm^6	129	129			127	127		
c_{+-}	129	129			98	98		
d_{++}	278	278			150	150		
d_{--} } $\times 10^{76}$ erg cm^8	260	260			266	266		
d_{+-}	250	250			177	177		
$C\times 10^{60}$ erg cm^6	1621	1105	5836	3978	1251	850	4378	2975
$D\times 10^{76}$ erg cm^8	2630	1751	9468	6304	1898	1254	6643	4389
$r_0\times 10^8$ cm (meas.)	3.553	3.430	3.553	3.442	3.339	3.227	3.339	3.230
$\beta\times 10^{12}$ barye^{-1}	5.9				5.602			
$\beta^{-1}(\partial\beta/\partial T)_P\times 10^4$ deg.$^{-1}$	6				14.6			
$\beta^{-1}(\partial\beta/\partial P)_T\times 10^{11}$ barye^{-1}	−0.30				−2.75			
$V^{-1}(\partial V/\partial T)_P\times 10^4$ deg.$^{-1}$	1.887				1.42			
R	1.82	1.08	1.82	1.51	1.19	2.01	1.19	1.04
S	124.9				113.7			
$\alpha e^2/r_0$ } $\times 10^{12}$ ergs per molecule	11.29	11.59	11.29	11.55	12.01	12.32	12.01	12.31
C/r_0^6	0.81	0.68	2.90	2.40	0.93	0.75	3.16	2.62
D/r_0^8	0.10	0.09	0.37	0.32	0.12	0.11	0.43	0.37
$\rho\times 10^8$ cm	0.290	0.290	0.365	0.365	0.319	0.319	0.374	0.374
b_1	28930	28930	5734	5734	6170	6170	3131	3131
b_2	28930	28930	4014	4014	6170	6170	1722	1722
$B_1(r_0)$ } $\times 10^{12}$ ergs per molecule	1.09	1.25	2.70	2.75	1.40	1.50	3.32	3.34
$B_2(r_0)$	0.12	0.02	0.31	0.07	0.21	0.05	0.34	0.10
U	10.99	11.09	11.55	11.45	11.42	11.63	11.94	11.86
ΔU	−0.10		0.10		−0.21		0.08	
$\Delta\Phi$ kcal./mole (calc.)	−1.4		1.4		−3.0		1.2	
$\Delta\Phi$ kcal./mole (meas.)	1.34		1.34		1.03		1.03	
$r_0\times 10^8$ cm 0°K (calc.)		3.386		3.399		3.159		3.202

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[17] M. Born, *Dynamik der Krystallgitter* (Leipzig 1923), p. 536, 548, 554; M. Born and M. Goeppert-Mayer, *Handbuch der Physik*, Vol. 24 (Berlin 1933), p. 630.

TABLE III. *Summations used to calculate the van der Waals forces.*

SUMMATION	SIGN OF IONS	LATTICE TYPE	
		CsCl	NaCl
$1/r^6$	like	3.5446	1.8067
	unlike	8.7088	6.5952
$1/r^8$	like	2.1977	0.8001
	unlike	8.1575	6.1457
$1/r^{10}$	like	1.5250	0.3847
	unlike	8.0394	6.0414
$(-1)^{l_1+l_2+l_3}3x^4/r^5$	both	1.8406[1]	−3.226[3]
$(-1)^{l_1+l_2+l_3}3x^2y^2/r^5$	both	−1.8016[2]	0.739
x^4/r^{10}	like	1.0200	0.3204
	unlike	1.0413	2.0972
x^2y^2/r^{10}	like	0.0808	0.1409
	unlike	0.9308	0.0506
x^4/r^{12}	like	0.6831	0.1376
	unlike	0.9236	2.0213
x^2y^2/r^{12}	like	0.0247	0.0646
	unlike	0.8978	0.0136
$r_0=$ unit length			

[1] M. Goeppert-Mayer and A. May, Phys. Rev. **50**, 99 (1936).
[2] M. Goeppert-Mayer and A. May, Phys. Rev. **52**, 242 (1937).
[3] Born, reference 17, p. 738.

tions $x=l_1a$, $y=l_2a$, $z=l_3a$, where a, for both the CsCl type and NaCl type lattices, is half the distance between nearest like ions. For the CsCl type all l's must be even or all odd.

The van der Waals contribution to c_{11} is

$$(c_{11})_v=-\frac{48}{\Delta}\left(\frac{c_{++}+c_{--}}{2}\sum_{\substack{\text{like}\\ \text{ions}}}\frac{x^4}{r^{10}}+c_{+-}\sum_{\substack{\text{unlike}\\ \text{ions}}}\frac{x^4}{r^{10}}\right)$$

$$-\frac{80}{\Delta}\left(\frac{d_{++}+d_{--}}{2}\sum_{\substack{\text{ilke}\\ \text{ions}}}\frac{x^4}{r^{12}}+d_{+-}\sum_{\substack{\text{unlike}\\ \text{ions}}}\frac{x^4}{r^{12}}\right). \quad (8)$$

As in calculating the lattice energies, only the first and second neighbors are included in the repulsion. We obtain

$$(c_{11})_r=(1/\Delta\rho^2)[(8/9)b_1r_0(r_0+\rho)e^{-r_0/\rho}$$
$$+2b_2ar_0(ar_0+\rho)e^{-ar_0/\rho}] \quad (9)$$

for the CsCl type lattice, and

$$(c_{11})_r=(1/\Delta\rho^2)[2b_1r_0(r_0+\rho)e^{-r_0/\rho}$$
$$+8^{\frac{1}{2}}b_2r_0(ar_0+\rho)e^{-ar_0/\rho}] \quad (10)$$

for the NaCl type.

Similarly we have

$$(c_{12})_r=(b_1/\Delta\rho^2)(8/9)r_0(r_0+\rho)e^{-r_0/\rho} \quad \text{(CsCl type)}, \quad (11)$$

$$(c_{12})_r=(b_2/\Delta\rho^2)\sqrt{2}r_0(ar_0+\rho)e^{-ar_0/\rho} \quad \text{(NaCl type)}. \quad (12)$$

Nothing is contributed to $(c_{12})_r$ by the first neighbors for the NaCl type, nor by the second neighbors for the CsCl type. The other components of c_{12} differ from the sum in c_{11} only in the substitution of the factor x^2y^2 for x^4.

The value of R needed for the calculation of c_{44} has already been obtained for the body-centered lattice. For the simple lattice it is calculated from Eq. (2).

The van der Waals sums were computed directly to spheres of radii seven times the lattice constant, integrated to infinity and then corrected by comparison with the inverse power

TABLE IV. *Elastic constants* × 10^{-11} *ergs/cm*^{3}.

	CsCl TYPE			NaCl TYPE		
	c_{11}	c_{12}	c_{44}	c_{11}	c_{12}	c_{44}
CsCl						
electrostatic	1.707	−1.671		−2.615	0.599	
van der Waals *C*	−3.453	−1.634		−4.021	−0.335	
van der Waals *D*	−0.681	−0.379		−0.972	−0.037	
repulsion	6.638	4.548		11.358	0.151	
$R/6\Delta$	0.044			0.031		
	4.255	0.864	0.908	3.781	0.378	0.409
NH₄Cl						
electrostatic	2.188	−2.142		−3.372	0.772	
van der Waals *C*	−4.585	−2.122		−5.302	−0.457	
van der Waals *D*	−0.966	−0.519		−1.355	−0.056	
repulsion	8.046	5.710		14.139	0.205	
$R/6\Delta$	0.035			0.023		
	4.718	0.927	0.962	4.133	0.464	0.487

summations of r of Jones and Ingham[9] by using the relation

$$3\sum\frac{x^4+2x^2y^2}{r^{n+4}}=\sum\frac{1}{r^n},\quad (n=6,\,8)$$

as was done by Herzfeld and Goeppert-Mayer.[18] The summations for like ions of the body-centered type are obtained, by a change of scale, from the like and unlike ion summations for the simple lattice.

The summations are given in Table III and the resulting constants in Table IV.

In averaging the sound velocities over all directions, the method of Born and Kármán[19] cannot be used since it requires that the quantity $(3c_{12}-c_{11})/(c_{11}-c_{12})$ be small. Herzfeld and Goeppert-Mayer[18] substituted a geometric mean for the average

$$3(1/w^3)_{\text{Av}}=(1/w_1^3)_{\text{Av}}+(1/w_2^3)_{\text{Av}}+(1/w_3^3)_{\text{Av}}$$

proposed by Debye. Because of the relatively small values of c_{12} and c_{44}, the several sound velocities will differ considerably and the geometric mean would be too high. The averages, $(1/w^3)_{\text{Av}}$, where w is the sound velocity, were obtained by the method of Hopf and Lechner[20] which is especially applicable to the case where c_{12} and c_{44} are small.

The acoustic frequency limit is found from Debye's formula

$$\nu_m{}^3=3/4\pi\Delta(1/w^3)_{\text{Av}}.$$

The velocity averages and corresponding frequencies calculated for 273° are given in Table V.

The frequencies corresponding to various temperatures may be of interest in connection with the calculation of the transition points, and a number of values are included in Table VI. In their computation the lattice constants obtained for these temperatures by means of the expansion coefficients, have been used.

TABLE V.

	$(1/w^3)_{\text{Av}}\times 10^{17}$ (cm/sec.)$^{-3}$		$\nu_m\times 10^{-12}$ sec.$^{-1}$	
	CsCl	NH₄Cl	CsCl	NH₄Cl
CsCl type	14.4	3.14	2.86	5.10
NaCl type	26.9	5.08	2.21	4.12

TABLE VI. *Elastic constants and acoustic frequency limits (ν_m) at various temperatures.*

	CsCl TYPE				*NaCl* TYPE			
	c_{11}	c_{12}	c_{44}	ν_m	c_{11}	c_{12}	c_{44}	ν_m
	$\times 10^{-11}$			$\times 10^{-12}$	$\times 10^{-11}$			$\times 10^{-12}$
CsCl								
0°K	4.820	1.205	1.205	3.18	4.606	0.392	0.392	2.24
135°	4.638	1.090	1.106	3.08	4.305	0.387	0.399	2.23
273°	4.254	0.864	0.908	2.86	3.781	0.378	0.409	2.21
718°	3.284	0.340	0.447	2.19	2.436	0.350	0.431	2.12
NH₄Cl								
0°K	5.104	1.179	1.179	5.50	4.684	0.474	0.474	4.12
273°	4.718	0.927	0.962	5.10	4.133	0.464	0.487	4.12
500°	4.340	0.692	0.758	4.67	3.565	0.455	0.501	4.04

Calculating these frequencies by the Hopf and Lechner method is a long task, but this may be obviated by using an approximation developed by Blackman.[21] His formula can be written

$$\nu_m=k[c_{11}(c_{44})^2\Delta]^{1/6}/M^{1/2} \tag{13}$$

where k is a constant and M is the molecular weight. From a number of frequencies previously calculated by the Hopf and Lechner method, the constant was found to have the value, $k=21.8$, for the elastic constants expressed in the unit 10^{11} ergs/cm^3, Δ in 10^{-23} cm^3, and ν_m in 10^{12} sec.$^{-1}$. Since the longer method involves the small differences of large quantities, the accuracy which it yields is generally poor, and since the deviations between results obtained by the two methods amount to only a few percent, the approximation appears quite satisfactory.

OPTICAL FREQUENCIES

The optical frequencies are derived by a method similar to that already described. Following Born[22] we first evaluate the D "bracket-symbols,"

$$D=\frac{1}{\Delta}\sum\left[\frac{1}{r}\frac{d\phi}{dr}+\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{d\phi}{dr}\right)x^2\right], \tag{14}$$

where the summation is over unlike ions only.

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[18] K. F. Herzfeld and M. Goeppert-Mayer, Phys. Rev. **46**, 995 (1934).

[19] M. Born and Th. von Kármán, Physik. Zeits. **14**, 15 (1913); Born, reference 17, p. 647.

[20] L. Hopf and G. Lechner, Verh. d. D. phys. Ges. **16**, 643 (1914); Born, reference 17, p. 649.

[21] M. Blackman, Proc. Roy. Soc. **A148**, 400 (1935).

[22] Born, reference 17, pp. 536, 568, 738, 740.

TABLE VII. *Optical frequencies (273°K). D (Born)×10⁻²⁶ ergs/cm⁵.*

LATTICE TYPE	*CsCl*		*NH₄Cl*	
	CsCl	NaCl	CsCl	NaCl
electrostatic	−1.975	−1.433	−2.901	−2.098
van der Waals *C*	−2.114	−1.776	−3.160	−2.640
van der Waals *D*	−0.595	−0.533	−0.942	−0.839
repulsion	7.658	6.648	10.721	9.063
frequencies ($\times 10^{-12}$)	2.974	2.906	3.718	3.486
	3.368	3.607	5.232	5.494

TABLE VIII. *Optical frequencies—various temperatures.* $D\times 10^{-26}$, $\nu_r\times 10^{-12}$.

	CsCl				*NH₄Cl*			
	CsCl type		NaCl type		CsCl type		NaCl type	
T°K	D	ν_r	D	ν_r	D	ν_r	D	ν_r
0	3.797	3.04	3.528	3.27	4.354	4.37	3.944	4.55
273	2.974	2.69	2.906	2.99	3.718	3.96	3.486	4.30
500					3.125	3.61	3.017	3.98
718	1.786	1.99	1.914	2.43				

Using Ewald's method, Born found for the electrostatic part

$$D_c = -4\pi e^2/3\Delta^2. \tag{14a}$$

The van der Waals contributions are:

$$D_v = \frac{6c_{+-}}{\Delta}\sum\frac{1}{r^8} - \frac{48c_{+-}}{\Delta}\sum\frac{x^2}{r^{10}} + \frac{8d_{+-}}{\Delta}\sum\frac{1}{r^{10}} - \frac{80d_{+-}}{\Delta}\sum\frac{x^2}{r^{12}},$$

where again the summations are limited to unlike ions. For both crystal types involved

$$3\sum\frac{x^2}{r^{n+2}} = \sum\frac{1}{r^n}, \quad (n=8,\ 10)$$

so that

$$D_v = -\frac{10c_{+-}}{\Delta}\sum\frac{1}{r^8} - \frac{56}{3}\frac{d_{+-}}{\Delta}\sum\frac{1}{r^{10}}. \tag{14b}$$

The summations over inverse powers of r are given by Jones and Ingham[9] and are listed in Table III.

Since only the interactions between unlike ions are included, the repulsion part contains only the first neighbors:

$$D_r = (bM/3\Delta\rho^2 r_0)(r_0 - 2\rho)e^{-r_0/\rho}. \tag{14c}$$

The frequencies were calculated from Born's formula, which assumes that they are monochromatic: $2\pi\nu = (\Delta D/m)^{\frac{1}{2}}$ m is the reduced mass of the ions, i.e. $1/m = 1/m_1 + 1/m_2$, where m_1 and m_2 are the masses of the two ions. The components of D for 273° and the corresponding frequencies are listed in Table VII.

The infrared absorption limit of CsCl as measured by Barnes[23] is 102.0 microns, corresponding to a frequency of 2.94×10^{12} sec.$^{-1}$. The value 3.37×10^{12} differs from this by fifteen percent.

Heckmann[24] has derived a formula for computing the effect on the frequencies, of the electron polarization which has been neglected in the method just used. This formula can be written

$$\nu_r^2 = \nu_\sigma^2 - \frac{e^2}{3\pi m\Delta}\,\frac{\alpha}{1-\alpha} \tag{15}$$

by putting $\beta = 1$ in the form given by Heckmann. ν_r is the actual maximum of absorption; ν_σ, the frequency which we have calculated from the elastic properties; e, the electronic charge; Δ, the volume per molecule; m, the reduced mass of the ions, and $\alpha = (n^2-1)/(n^2+2)$ is the electronic polarizability, n being the visible refractive index. For optical frequencies the index of refraction of the CsCl type lattice is practically the same[25] for CsCl and NH_4Cl, and in both cases we have used $n = 1.620$, obtained for CsCl by Born and Heisenberg[26] by extrapolation to zero frequency.

We find for CsCl, $\nu_\sigma^2 - \nu_r^2 = 4.11\times 10^{24}$ and $\nu_r = 2.69\times 10^{12}$ sec.$^{-1}$, which differs from Barnes' value by eight percent.

The optical frequencies corresponding to a number of temperatures are included in Table VIII. ν_r was calculated on the assumption that α is inversely proportional to Δ, and that in other respects the value of α for the NaCl type lattice is the same as for the CsCl type.

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The Transition Temperature

The transition temperature is now calculated from the equality of the free energies.

Because of the high temperatures involved, the free energies can be computed from two expressions of the form

$$F=-NU+3RT \ln h\nu_m/kT+3RT \ln h\nu_r/kT,$$

where ν_m and ν_r are the acoustic and optical frequencies, h is Planck's constant and k the gas constant per molecule.

The temperature at which the free energies are equal is given by

$$T=\frac{(U_1-U_2)}{3k \ln (\nu_m\nu_r)_1/(\nu_m\nu_r)_2}, \qquad (16)$$

where the subscripts 1 and 2 refer to the CsCl type and NaCl type lattices, respectively.

By using the frequencies calculated for 0°K, the transition temperatures obtained are 810°K for CsCl and 700°K for NH_4Cl, as compared with the experimental values, 718° and 457°. These results must be regarded as satisfactory in view of the small accuracy to be expected. Slightly better values are obtained if the corrections for the electron polarization are not made.

In calculating the transition temperatures from Eq. (16), the frequencies used should be those corresponding to the temperature T.

Because of the rapid decrease of ν_m for the CsCl type lattice as indicated in the values of Table VI, no transition point is obtained if the temperature dependence of the frequencies is considered. It appears quite probable that it is the temperature dependence of the frequencies that is incorrect rather than the values found for absolute zero.

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Coercive Force in Single Crystals

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The coercive force H_c of ten single crystal disks of silicon-iron has been measured in different directions in their planes. In any one disk, H_c changes with the direction; it is mainly determined by the angle α_3 between the field and the [001] axis nearly normal to the disk, and has a minimum value when that angle is 90°. The angle α_1 between the field direction and another cubic axis which lies nearly in the plane of the disk and close to the field direction has a smaller effect on H_c. The relation $H_c=A/\cos\alpha_1+B\cos\alpha_3$ represents very closely the curves taken on well annealed disks; A and B are constants with values close to 0.1 and 0.4, respectively. The effect on H_c of varying the disk shape and of increasing the internal strains by carburization has been studied. Finally it has been shown that H_c values calculated from the empirical relation are in good agreement with data on single crystal wires and strips (Kaya, Ruder).

1. Introduction

Magnetic theory can at present account satisfactorily for the behavior of ferromagnetic material near technical saturation. Our understanding, on the other hand, of what happens in low fields in general, and of the phenomenon "coercive force" in particular, is still very limited and vague. It was recognized early that internal strains in a ferromagnetic material caused by cold work or by impurities increased the coercive force. This was proved systematically by Kussmann and Scharnow.[1] Contributions from the theoretical side were made by R. Becker, N. Akulov and by F. Bloch. Bloch[2] in referring to experiments by K. J.

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