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On the Thermal Expansion Coefficient of Crystalline Substances.

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The purpose of the present paper is to elucidate the mechanism of thermal expansion of crystalline substances and its variation on the ground of M. Born and A. Landé's ionic lattice theory⁽¹⁾ and the quantum theory.

1. Thermal expansion coefficients of diatomic crystals.

According to Born's view, the binary compounds, for instance alkaline halides, have such a construction that an alkaline atom gives one electron to a halogen atom and they attract each other in consequence of the electrostatic forces between these ionic charges, and besides they are acted by the repulsive force due to the surrounding bound electrons of each atom, which is not purely electrostatical but some part surely electrodynamical, and by the joint action of these two kinds of forces all atoms distribute themselves in a definite equilibrium positions; and the atomic lattice-structure constructed in this way is what may be analysed by means of X-rays.

(1) M. Born and A. Landé, *Sitzungsber. d. Preuss. Akad. d. Wiss.*, 1048, 1918, *Verh. d. D. Phys. Ges.* 19, 210, 1918, " 20, 210, 1918, A. Landé, " 20, 217, 1918, Born and Landé, " 20, 202, 1918, Born, " 20, 230, 1918, " 21, 13, 1919, " , " , 21, 199, 533, 1919, M. Born, *Ann. d. Phys.* 61, 87, 1919, Born, *Verh. d. D. Phys. Ges.* 21, 679, 1919, E. Bormann, *Zeitschr. f. Phys.* 1, 55, 1920, K. Fajans and K. F. Herzfeld, *Zeitschr. f. Phys.* 2, 309, 1920, A. Smakel, *Zeitschr. f. Phys.* 1, 309 1920, T. Rella, *Zeitschr. f. Phys.* 3, 157, 1920, W. Schottky, *Phys. Zeit.* 21, 232, 1920, H. Schwendenwein, *Zeitschr. f. Phys.* 4, 73, 1921, M. Born, and E. Brody, *Zeitschr. f. Phys.* 7, 217, 1922, O. Eersleben, *Phys. Zeit.* 24, 73, 97, 1923.

By the above considerations, Born and Landé⁽¹⁾ obtained the following formula for compressibility

$$K = \frac{9 \delta^4}{(n-1)a}, \quad (1)$$

where δ is the length of the side of the elementary cube which represents a complete crystallographic unit (Fig. 1). a is the Madelung's

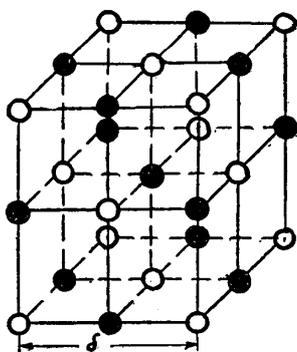


Fig. 1

constant⁽²⁾ whose value is $13.94e^2$ for alkaline halides (e is the charge of an electron) and this value of a can be applied to all crystals having similar lattice. And n is the constant which characterizes the repulsive force between any two atoms in the way that it is inversely proportional to the n th power of the distance of their centers, and Born and Landé showed that $n=9$ for alkaline halides from the investigation of compressibility. The electric charge

per elementary cube in which four molecules are contained, is $-\frac{a}{\delta} + \frac{b}{\delta^n}$,

and accordingly the energy per one mol is

$$F = \frac{N}{4} \left(-\frac{a}{\delta} + \frac{b}{\delta^n} \right), \quad (2)$$

where N is Avogadro's number and equals to 6.06×10^{23} . But, at any temperature, except the absolute zero point, the atoms are not in rest but are oscillating with their natural frequencies about their positions of equilibrium, and it may be said that Born and Landé's calculations are satisfied only at absolute zero temperature, for they assumed that atoms are always in rest. Thus if we write δ_0 for the value of δ at absolute zero point, the condition of equilibrium is

$$\left(\frac{\partial F}{\partial \delta} \right)_{T=0} = 0 \quad \text{i.e.,} \quad b = \frac{a \delta_0^{n-1}}{n}. \quad (3)$$

(1) M. Born and A. Landé, *Verh. d. D. Phys. Ges.* **20**, 210, 1918.

(2) Madellung, *Phys. Zeit.* **19**, 524, 1918.

Now, at any temperature T , when atoms are oscillating, this condition holds no longer and it will be roughly supposed that the force $-\frac{\partial F}{\partial \delta}$ is balanced with the repulsive force due to impact. So, we must regard $\frac{\delta}{2}$ as the mean central distance between two nearest atoms. In other words, the above energy is the part of the potential energies, independent of oscillations.

E. Grüneisen,⁽¹⁾ in 1912, obtained from the atomic considerations the characteristic equation (Zustand gleichung) of monoatomic crystalline substances, that was

$$pv + F_v'v = \gamma E. \quad (4)$$

We can however extend this relation to binary compounds, because the assumption on atomic force in his theory is very general, and not restricted to monoatomic. Here, F is the potential energy independent of thermal oscillations and indeed equals to (2). Its suffix v and dash mean the operation of the differentiation with respect to its volume v per one mol. p is the external pressure acting uniformly on the surface of the crystal. γ is a constant related to the force function, and does not vary with pressure and temperature, and E is the energy of thermal oscillations per one mol.

Consider the isopiestic change and put $p=0$, then from (4) we have

$$F_v' \cdot v = \gamma E. \quad (5)$$

In order to calculate F_v' , transform (2) in terms of v , then

$$F = \frac{n}{4} \left\{ -\frac{a}{\left(\frac{4}{N}\right)^{\frac{1}{3}} v^{\frac{1}{3}}} + \frac{b}{\left(\frac{4}{N}\right)^{\frac{n}{3}} v^{\frac{n}{3}}} \right\}, \quad (6)$$

because $\delta = \left(\frac{4}{N}\right)^{\frac{1}{3}} v^{\frac{1}{3}}$.

Differentiate (6) with respect to v and express the result in terms of δ ,

(1) E. Grüneisen, *Ann. d. Phys.* **39**, 257, 1912 and the same formula was obtained by S. Ratnowsky, *Ann. d. Phys.* **38**, 637, 1912

$$F_v' = \frac{N}{12 \cdot v} \left\{ \frac{a}{\delta} - \frac{nb}{\delta^n} \right\}.$$

Hence we shall have for (5)

$$\frac{N}{12} \left\{ \frac{a}{\delta} - \frac{nb}{\delta^n} \right\} = \gamma E. \quad (7)$$

Differentiating this equation with respect to T , we obtain

$$\frac{N}{12 \delta^2} \left\{ -a + \frac{n^2 b}{\delta^{n-1}} \right\} \frac{d\delta}{dT} = \gamma \left(\frac{dE}{dT} \right)_p,$$

and making use of equation (3) and the relation $\frac{d\delta}{dT} = \alpha \delta$, where α is the expansion coefficient at temperature T , we have

$$\frac{N\alpha a}{12\delta} \left\{ -1 + n \left(\frac{\delta_0}{\delta} \right)^{n-1} \right\} = \gamma \left(\frac{dE}{dT} \right)_p. \quad (8)$$

If the temperature is not very high, we may put approximately $\frac{\delta_0}{\delta} = 1$.

And finally, the formula for the expansion coefficient is obtained, that is

$$\alpha = \frac{12 \delta \gamma}{N a (n-1)} \left(\frac{dE}{dT} \right)_p. \quad (9)$$

From this formula we see that the ratio of α to $\left(\frac{dE}{dT} \right)_p$, *i. e.*, to nearly⁽¹⁾ the specific heat at constant pressure per mol. (or to the molecular heat at constant pressure) is independent of T , at least, at comparatively lower temperature, this relation was already remarked by many observers especially by Grüneisen⁽²⁾ on various substances.

The oscillation-energy E is complicated in case of binary com-

(1) Strictly speaking, $\left(\frac{dE}{dT} \right)_p$ is not the molecular heat at constant pressure. The latter is the sum of the elastic work for expansion and the former. But the lower the temperature falls, the nearer they are.

(2) Grüneisen, Ann. d. Phys. (4) **55**, 371, 1918, **58**, 753, 1919.

pounds. Born and Kármán⁽¹⁾ investigated it under a special assumption and obtained the following expression

$$E = NkT \left\{ \sum_{j=1}^3 3 \left(\frac{T}{\Theta_j} \right)^3 \int_0^{\frac{\Theta_j}{T}} \frac{z^3}{e^z - 1} dz + \sum_{j=4}^6 \frac{\frac{\Theta_j}{T}}{e^{\frac{\Theta_j}{T}} - 1} \right\}. \quad (10)$$

The three terms in the first summation have the form of Debye's universal function and the characteristic temperature Θ_1 , Θ_2 , and Θ_3 in them have been calculated by using mean elastic constants; while the three terms in the second summation have the form of Einstein's function and depend solely on the natural oscillations of atoms, that is, Θ_4 , Θ_5 and Θ_6 are the characteristic temperatures for three natural frequencies. But, for the sake of simplicity we will use one of Einstein's formulæ⁽²⁾ with the mean frequency of natural oscillations of atoms. That is

$$E = 2N \frac{3 h \nu_m}{e^{\frac{h \nu_m}{kT}} - 1}. \quad (11)$$

And yet ν_m depends⁽³⁾ on the atomic force due to the surrounding other atoms and if their distances vary the force will be changed and consequently ν_m must be shifted according as the temperature varies. But, as this shift is very small, we shall neglect the term dependent on $\frac{d\nu_m}{dT}$. Thus from (9) and (11) we obtain

(1) At first M. Born and Th. v. Kármán investigated E for elementary substances. *Phys. Zeitschr.* **13**, 297, 1912, **14**, 15, 65, 1913. By H. Thirring their result was extended into the series calculable easily for higher temperature. *Phys. Zeitschr.* **14**, 867, 1913. On the other hand, for lower temperature, Born and Kármán deduced its approximate formula. And afterwards, Thirring extended their calculation for mehratomic substances. *Phys. Zeitschr.* **15**, 127, 180, 1914. And (10) was quoted from p. 77 in M. Born's book i. e., *Dynamik der kristallgitter*, (B.G. Teubner, 1915)

(2) A. Einstein, *Ann. d. Phys.* **22**, 180, 1907.

(3) Debye marked at first that $h\nu_m$ must be the function of temperature. *Archives des Sciences Phys. et. Naturelles* **32**, 1911. I will discuss this point in another

$$\alpha = \frac{72 \delta \gamma k}{a(n-1)} \frac{e^{\frac{h\nu_m}{kT}} \left(\frac{h\nu_m}{kT}\right)^2}{\left(e^{\frac{h\nu_m}{kT}} - 1\right)^2}, \quad (12)$$

or by (1)

$$\alpha = \frac{8 K \gamma k}{\delta^3} \frac{e^{\frac{h\nu_m}{kT}} \left(\frac{h\nu_m}{kT}\right)^2}{\left(e^{\frac{h\nu_m}{kT}} - 1\right)^2}, \quad (12a)$$

or

$$= \frac{K \gamma}{3 \nu} \left(\frac{dE}{dT}\right)_p, \quad (12b)$$

(12_b) gives facilities for finding α from the observed values of K , ν and $\left(\frac{dE}{dT}\right)_p$; thus although a and n are unknown α can be found.

We must however notice that γ should be selected suitably for each of all substances. At first, we consider halogen salts putting $\gamma = \frac{3}{2} = 1.5$, and as the value of the frequency ν_m we may use the mean frequency residual rays, and thus we obtain the calculated values of $\alpha^{(1)}$ as follows:

(1) In order to calculate by Born's formula (10), we may use H. Thirring's formula for comparatively higher temperature, that is mean atomic heat

$$\bar{C}_v = \frac{1}{2} \left(\frac{dE}{dT}\right)_v = 3R \left\{ 1 - \frac{B_2}{2^1} J_1 \left(\frac{\beta'}{T}\right)^2 + 3 \frac{B_4}{4^1} J_2 \left(\frac{\beta'}{T}\right)^4 - \dots \right\} \dots \dots (10a)$$

where B_2, B_4, \dots are Bernoulli's numbers, and their values are

$$B_2 = -\frac{1}{6}, \quad B_4 = \frac{1}{30}, \dots \dots$$

and J_1, J_2, \dots are calculated from the mean elastic constants.

	NaCl	KCl	CaF ₂
$J_1 \times 10^{-52}$	1.86	1.39	5.33
$J_2 \times 10^{-50}$	4.24	2.43	3.48

and $\beta' = \frac{h}{k}$. On the other hand, from (11)

$$C_v = \frac{3 e^{\frac{h\nu_m}{kT}} \left(\frac{h\nu_m}{kT}\right)^2 kN}{\left(e^{\frac{h\nu_m}{kT}} - 1\right)^2} \quad (11a), \quad kN = R$$

Compare the values of \bar{C}_v at $T = 313$ from (11_a) and (10_a)

(to be continued)

	$\nu_m \times 10^{-12}$	$\delta \times 10^8$	$\alpha \text{ cal.} \times 10^5$	$\alpha \text{ obs.} \times 10^5$	T
NaCl	5.77	5.63	3.87	4.039	313
KCl	4.73	6.26	3.50	3.8026	„
KBr	3.63	6.60	3.81	4.2007	„
KI	3.19	7.11	4.11	4.2653	„
AgCl	3.68	5.56	3.17	3.294	„
AgBr	2.66	5.76	3.33	3.4687	„

Then we can find the lattice distance at any temperature from the observed value at room temperature. And as

$$\delta = \delta_0 \left(1 + \int_0^T \alpha dT \right),$$

it follows that

$$\frac{\delta}{\delta_0} = 1 + \frac{72 \delta \gamma_k}{\alpha (n-1)} \frac{h\nu_m}{e \frac{h\nu_m}{kT} - 1} \quad (13)$$

For instance, the ratio $\frac{\delta_{313}}{\delta_0}$ and $\frac{\delta \text{ melting point}}{\delta_0}$ are shown in the following table:

	(11a)g. cal.	(10a)g. cal.	
NaCl	5.57	5.72	} J. i.e., Joule's equivalent heat = 4.180×10^7
KCl	5.74	5.79	
CaF ₂	4.99	5.38	

From these values α_s . cal. by (10a) (11a) are as follows :

	NaCl	KCl	CaF ₂
$\alpha (10a) \times 10^5$	3.97	3.53	2.06
$\alpha (11a) \times 10^5$	3.87	3.50	1.97
$\alpha \text{ obs.} \times 10^5$	4.04	3.80	1.91

	δ_{313}/δ_0	δ_m/δ_0	Melting point T_m
NaCl	1.00638	1.0311	1073 (800° C)
KCl	1.00782	1.0343	1043 (770° C)
KBr	1.00911	1.0359	1023 (750° C)
KI	1.0100	1.0371	ca 941 (668° C)
AgCl	1.00758	1.0211	733 (460° C)
AgBr	1.00855	1.0213	700 (427° C)

It may be seen from these results that the ratios of expansion at 40° C are fairly different for various salts, but at melting point its values for alkaline halides are nearly equal to 0.035 and for Ag-halides 0.021, this difference seems to depend on the difference of the atomic volume between these metals.

Next, we will apply (12) to fluorite. By Landé⁽¹⁾ and Bormann⁽²⁾ it has been shown that $n=7.20$ calculated from its compressibility and that the ionic charge of F-atom (●) is -e, that of Ca-atom (○) is +2e (Fig. 2.) and $a=46.93e^2$.

	$\nu_m \times 10^{-12}$	$\delta \times 10^8$	$\alpha \text{ cal.} \times 10^5$	$\alpha \text{ obs.} \times 10^5$	T	γ
CaF ₂	9.49	5.46	1.96	1.9115	313	3

(1) A. Landé, Verh. d. D. Phys. Ges. **20**, 217, 1918.

(2) E. Bormann, Zeitschr. f. Phys. **1**, 55, 1920

2. Thermal expansion coefficients of elementary substances.

We will proceed to investigate the expansion coefficients in case of monoatomic crystalline substances. There are many of this kind which have been analysed by means of X-rays. Among the different kinds of lattices thus revealed, those belonging to the cubic system are the following three: (I) face-centered lattice, (II) body-centered lattice, (III) diamond lattice.

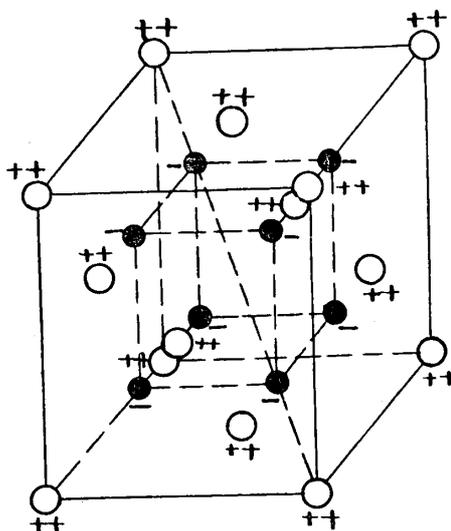


Fig. 2.

At first, we must consider by what forces the atoms constituting these lattices are in equilibrium. According to recent development of the theory of matter, these forces have necessarily electrical origin. Then in elementary substances, especially metals, all atoms must be in the similar state, electrical or otherwise. Referring to the analogy of the state of solution, it is conceivable that every metallic atom has a positive electric charge. If so, what will be the carriers of the corresponding negative charges? I think that they are free electrons which sit at the unstable positions among atoms and move always irregularly by thermal agitation. On the contrary, in dielectric substances, one of the atoms gives the electrons corresponding to its valency to another atom, just like halogen salts; and thus, the positive and negative atoms distribute themselves in the definite lattice points; these cases we need not to discuss further. In metals, the free electrons may move about, but we may assume that the average position of each electron corresponds to one of the lattice points proper to these electrons. In other words, in views of estimating the distributions of mean external electric field in the lattice, we may arrange the electrons suitably among the atomic lattice so as to form, as a whole an ionic lattice with the positive atoms. If such be

the case, what will be the mean positions of the free electrons? For this problem, we must infer the solution from the various characteristic properties of free electrons, among which the expansion coefficient also plays a significant rôle.

According to the electron theory, the number of free electrons is of the same order as the number of atoms. Besides they must be distributed in cubic symmetry, for all properties of the crystals belonging to the above lattices show this symmetry. Based on these two conditions, we may make a suitable assumption about the positions of electrons. If the theoretical values of the thermal expansion coefficient and compressibility of the assumed lattice agree well with the experimental values, we may consider the assumption made as justified.

Now, for the elementary substances, the energy of oscillations is

$$E = N \cdot \frac{3 h\nu_m}{e^{\frac{h\nu_m}{kT}} - 1} \quad (14)$$

Accordingly,

$$\alpha = \frac{36 \gamma \delta k}{(n-1)a} \frac{e^{\frac{h\nu_m}{kT}} \left(\frac{h\nu_m}{kT} \right)^2}{\left(e^{\frac{h\nu_m}{kT}} - 1 \right)^2}, \quad (15)$$

or

$$\alpha = \frac{4 K \gamma k}{\delta^3} \frac{e^{\frac{h\nu_m}{kT}} \left(\frac{h\nu_m}{kT} \right)^2}{\left(e^{\frac{h\nu_m}{kT}} - 1 \right)^2}. \quad (15a)$$

Or, otherwise, if we use Debye's function⁽¹⁾ which is

(1) P. Debye, Ann. d. Phys. **32**, 789, 1912. Also, if we use Born and Kármán's formula

$$E = N_g \frac{1}{(2\pi)^3} \sum_{k=1}^3 \int_0^{2\pi} \int \int f(\nu_k) d\varphi d\psi d\chi$$

(to be continued)

$$E = 9 kT \left\{ \frac{T}{\Theta} \right\}^3 N \int_0^{\frac{\Theta}{T}} \frac{z^3 dz}{e^z - 1}, \quad (16)$$

we obtain

$$\alpha = \frac{12 \gamma \delta}{(n-1)a} \frac{d}{dT} \left\{ 9 kT \left(\frac{T}{\Theta} \right)^3 \int_0^{\frac{\Theta}{T}} \frac{z^3 dz}{e^z - 1} \right\}. \quad (17)$$

In 1913 Debye⁽²⁾ obtained from his theory of elastic continuum the following formula for expansion coefficients of elementary substances

$$\alpha = \frac{a' K_0}{3 V_0} \frac{d}{dT} \left[9 kTN \left\{ \left(\frac{T}{\Theta_0} \right)^3 \int_0^{\frac{\Theta_0}{T}} \frac{z^3 dz}{e^z - 1} + \frac{1}{2} \frac{\Theta_0}{T} \right\} \right], \quad (18)$$

where V_0 , K_0 , Θ_0 are the volume of one mol, the compressibility and the characteristic temperature at zero point, and a' is the numerical coefficient in the following expansion of Θ ,

$$\Theta = \Theta_0 \left\{ 1 - a' \frac{\Delta}{V_0} + \frac{b'}{2} \frac{\Delta^2}{V_0^2} + \dots \right\}, \quad (19)$$

where Δ is the increment of volume in the interval from 0 to T . As the order of $\frac{\Delta}{V_0}$ is nearly 10^{-2} even if T equal to 10^3 and a' is 2 or 3,

we may put approximately $\Theta \doteq \Theta_0$; then (18) becomes

$$\alpha = \frac{a' K_0}{3 V_0} \frac{d}{dT} \left[9 kTN \left\{ \left(\frac{T}{\Theta} \right)^3 \int_0^{\frac{\Theta}{T}} \frac{z^3 dz}{e^z - 1} \right\} \right],$$

while as

$$K_0 = \frac{9 \delta_0^4}{a (n-1)}, \quad V_0 = \frac{N}{4} \delta_0^3$$

where φ , ψ , χ are the quantities depending on the velocities of propagation of elastic waves, and ν_1 , ν_2 , ν_3 are the three roots of the dispersion-equation $\Delta(\varphi, \psi, \chi, \nu) = 0$, and $f(\nu)$ is an Einstein's energy formula, N_g is the number of lattice points. But C_v from this formula coincides very closely with C_v from Debye's formula; which were verified by Born and Kármán, and Thirring.

(2) P. Debye, Phys. Zeitschr. **14**, 259, 1913, Wolfskehl-Kongretz, Göttingen 1913 (B. G. Teubner, Leipzig 1913)

the above formula will become

$$\alpha = \frac{12 \delta_0 a'}{a(n-1)} \frac{d}{dT} \left\{ 9 kT \left(\frac{T}{\Theta} \right)^3 \int_0^{\frac{\Theta}{T}} \frac{z^3 dz}{e^z - 1} \right\}. \quad (20)$$

Compare this formula with (17), then we see that there may be the relation $\gamma = a'$. Debye calculated a' from the observed values of K and α of copper and obtained $a' = 1.9$. Accordingly γ equals nearly 2 for *Cu*.

(i) Face-centered lattice.

At first, we will calculate the values of γ from the expansion coefficients of metals belonging to the face-centered lattice by means of (15a).

	⁽¹⁾ $\nu_m \times 10^{-12}$	T	⁽²⁾ $K \times 10^{12}$	$\delta \times 10^8$	α obs. $\times 10^5$	α ca. $\times 10^5$	γ
Al	6.7	336	1.36	4.06	2.33	2.08	2.05
Cu	5.7	323	0.74	3.60	1.698	1.65	2.00
Ni	6.7	531 (mean)	0.57	3.53	1.516	1.51	2.17
Pd	5.2	323	0.57	3.90	1.1186	1.26	2.5
Pb	2.2	323	2.0	4.91	2.948	2.61	2.9
Ag	4.1	400 (mean)	0.92	4.06	1.95	1.93	2.6
Au	3.8	323	0.60	4.07	1.451	1.44	3.0
Pt	4.6	323	0.40	4.01	0.907	1.07	3.3

Then, γ is the function of molecular force and we obtain it by the same method as Grüneisen, that is $\gamma = \frac{4+n^{(3)}}{6}$. From this relation

(1) In this calculation I adopted as ν_m the values from Einstein's formula that is

$$\nu_m = \frac{\sqrt{6}}{2\pi} \left\{ \frac{\pi}{6} \right\}^{\frac{1}{3}} N^{\frac{1}{3}} M^{-\frac{1}{3}} \rho^{-\frac{1}{6}} K^{-\frac{1}{2}}.$$

Ann. d. Phys. (4), **34**, 170, 1911, **35**, 679, 1911.

(2) These values of K are quoted from Grüneisen, Ann. d. Phys, **22**, 838, 1907, **25**, 845, 1908.

(3) It seems that this relation does not strictly hold for binary compounds.

$n=6\gamma-4$. For the above substances, the values of n are calculated as follows :

	Al	Cu	Ni	Pd	Pb	Ag	Au	Pt
n	8.3	8.0	9.0	11	13	11.6	14	14

On the other hand, from (I)

$$a(n-1) = \frac{9\delta^4}{K} ;$$

by this formula we obtain the values of $a(n-1)$ for each metals.

	Al	Cu	Ni	Pd	Pb	Ag	Au	Pt
$a(n-1) \times 10^{17}$	1.80	2.04	2.29	3.65	2.62	2.66	4.12	5.82

From these values of $a(n-1)$ and n , we obtain the values of a which are tabulated as follows :

(1)	Al	Cu	Ni	Pd	Pb	Ag	Au	Pt	mean
a	$10.7 e^2$	$12.8 e^2$	$12.6 e^2$	$16.1 e^2$	$9.58 e^2$	$11.0 e^2$	$13.9 e^2$	$17.0 e^2$	$13.0 e^2$

The values of a for all of the above metals are nearly equal and are near $13.94 e^2$. This means nothing but that the ionic lattice constructed by positive atoms and electrons is very close to that of the halogen salt (in Fig. 1, consider, for instance, ● as electron, ○ as atom). Thus, in these metals the number of free electrons is equal to the number of atoms.

(ii) Body-centered lattice

The values of γ obtained from α are as follows :

(1) The absence of perfect coincidence may be explained by reason of the assumption of mean structure and the errors of observed values of K . The correctness of the former reason may be seen from the better coincidence for the substances having higher melting point, because for these substances the positions of electrons are not so much disturbed at the ordinary temperature.

	$\nu_m \times 10^{-12}$	T	$K \times 10^{12}$	$\delta \times 10^8$	$\alpha \text{ obs.} \times 10^5$	$\alpha \text{ cal.} \times 10^5$	γ
Fe	6.5	313	0.60	2.87	1.19	1.29	1
Na	2.53	298 (m.)	15.4	4.30	7.2	7.8	0.8
K	1.51	298 (m.)	31.5	5.20	8.3	8.4	0.8

From these values of γ we can calculate n .

	Fe	Na	K
n	2	1.2	1.2

Then, from K by means of (1),

	Fe	Na	K
$a(n-1) \times 10^{17}$	1.01	0.200	0.209

Thus we obtain the values of a from the above two data, as follows:

	Fe	Na	K
a	$44.7 e^2$	$43.8 e^2$	$45.9 e^2$

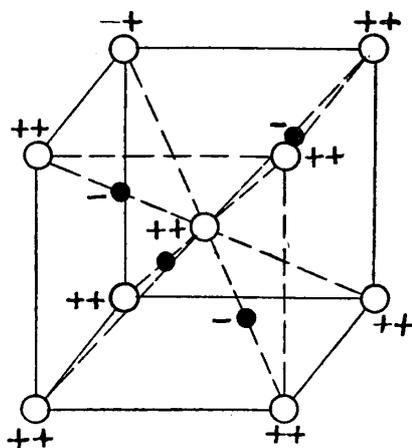


Fig. 3.

From these values of a it will be concluded that, as the lattice atoms are supposed to be body centered, the mean ionic lattice-structure of the above substances is similar to that of Cu_2O shown in Fig. 3, whose value of a equals to $47.8 e^2$. (in Fig. 3, ● electrons, ○ atoms.) Thus the ionic charges of an atom are $+2e$, and the number of electrons is twice the number of atoms. Considering their

electrical conductivity, it seems that some parts of these electrons are not free.

(iii) Diamond-lattice.

The observed values of K for diamond are as follows :
 0.5×10^{-12} by Richards, Zeit. Phys. Chem. 61, 1907,
 0.18×10^{-12} by L. H. Adams and E. D. Williamson, Journ. of Franklin Inst. 195, 492, 1923.

As this difference is large, we will use the weighted mean, assuming twice as much weight on Adams and Williamson's value as that on Richards, that is

$$K_{\text{mean}} = 0.3 \times 10^{-12}$$

At first, calculate γ from α .

	$\nu_m \times 10^{12}$	T	$\delta \times 10^8$	$\alpha \text{ obs.} \times 10^5$	$\alpha \text{ cal.} \times 10^5$	γ
C	24.0	323	3.55	0.118	0.153	1

From this value of γ , we have $n=2$.

Then from K , $a(n-1) = 52.8 \times 10^{-17}$, therefore

$$a = 59 \times (2e)^2. \text{ (1)}$$

Well, if we consider the case of zinc blende (ZnS), whose value of a equals to $60.5 e^2$, we see that the ionic lattice of diamond is the same as that of ZnS and there are two sorts of ionic atoms : the charge of one being $+4e$, and that of the other $-4e$ (Fig. 4).

3. Thermal variation of expansion coefficients.

By the above discussions, we have found that our formula expresses the experimental fact that α is proportional

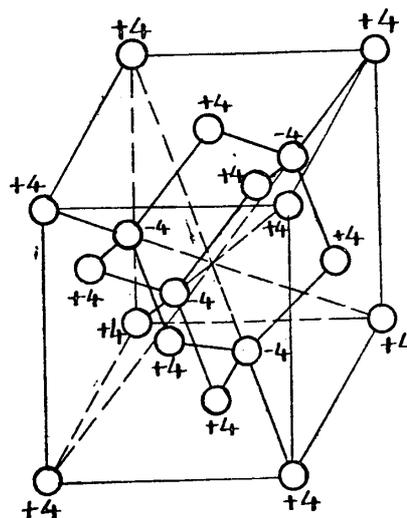


Fig. 4.

(1) The factor 2 means that the charge of Zn or S .

to $\left(\frac{dE}{dT}\right)_p$. Then we will calculate the values of α corresponding to various temperatures for some substances and compare them with their experimental values. In order to account for the thermal variation by (15), the value of the constant involved is selected so as to obtain coincidence at one particular temperature and then its variations are calculated.

(1) *Aluminium*

Al	T	α cal. $\times 10^5$	α obs. $\times 10^5$
	103	1.21	1.36
	133	1.61	1.56
	173	1.91	1.86
	213	2.03	1.99
	253	2.20	2.16
	336	<u>2.33</u>	<u>2.33</u>
	289—523	2.38	2.44
	523—648	2.44	2.70
	648—773	2.46	2.98

{ made to coincide at this temperature.

From this table, we see that (15) shows a discrepancy at temperatures higher than 336. This is due perhaps by the reason of neglecting the term containing $\frac{d\nu_m}{dT}$ and the supposition of the equality of $\frac{\delta_o}{\delta}$ to 1. The defect of the latter, however, can be approximately avoided as follows.

By (8)

$$\alpha = \frac{\left[n \left\{ \frac{\delta_o}{\delta} \right\}^{n-1} - 1 \right] \bar{\alpha}}{n-1},$$

where $\bar{\alpha}$ is the value given by (15) and α is the corrected value.

Then, as $\delta = \delta_0 (1 + \int_0^T \alpha dT)$, we shall have for the above equation ;

$$\alpha = \frac{\bar{\alpha}}{1 - n \int_0^T \bar{\alpha} dT}$$

So, consider the matter at two temperatures T_1 T_2 then the ratio of α will be

$$\frac{\alpha_{T_2}}{\alpha_{T_1}} = \frac{\bar{\alpha}_{T_2} / \bar{\alpha}_{T_1}}{1 - n \int_{T_1}^{T_2} \frac{\bar{\alpha}_{T_1} + \bar{\alpha}_{T_2}}{2} dT}$$

By this formula, the corrected values for high temperatures are as follows :

	289—523	523—548	648—773
α cal. $\times 10^5$	2.40	2.56	2.64
α obs. $\times 10^5$	2.44	2.70	2.96

(2) *Copper*

Cu	T	α cal $\times 10^5$	α obs. $\times 10^5$
	103	1.04	1.04
	123	1.24	1.21
	143	1.35	1.31
	163	1.43	1.44
	183	1.47	1.47
	203	1.55	1.50
	223	1.59	1.59
	243	1.62	1.61
	263	1.66	1.61
	283	1.68	1.63
	323	<u>1.70</u>	<u>1.70</u>
	289/523	1.74	1.72
	523/648	1.78(1.85)	1.86
	648/737	1.80(1.90)	1.96

made to coincide

The values in the bracket are the corrected ones. There is a fairly good agreement between the theoretical and the experimental values.

4. Structural difference of metals and dielectrics.

From the above investigations, it will be seen that the atoms of the dielectric substances either diatomic or monoatomic have the ionic charges corresponding to their valencies respectively. Accordingly, the electronic structure of each atom-ion is the same as the one of the neighbouring zero valence atom. For instance, consider rocksalt, the normal state of Na- and Cl-atom, by Bohr's consideration, have the following electronic structures.

$n_k : \dots\dots\dots$	1_1	2_1	2_2	3_1	3_2	}	$n = \text{total quantum numbers}$
Na no. of electrons.	2	4	4	1			$l = \text{azimutal } ,,$
Cl ,,	2	4	4	4	3		,,

Therefore, that of Na⁺ is

no. of electrons	2	4	4
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which corresponds to that of Neon atom.

And for Cl⁻

no. of electrons	2	4	4	4	4
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which corresponds to that of Argon atom.

Next, in the case of diamond, the normal state of C-atom is

no. of electrons	2	4
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Therefore, for C⁺⁺⁺ its electronic structure is

no. of electrons.	2
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this corresponds to the structure of Helium atom, for C⁻⁻⁻⁻

2	4	4
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corresponding to the structure of Neon atom,

in the case of Ca F ₂ ,	$n_k : \dots\dots\dots$	1_1	2_1	2_2	3_1	3_2	3_3	4_1
normal state of Ca-atom		2	4	4	4	4		2
,, ,, ,, F ,,		2	4	3				

Therefore

electronic state of Ca ⁺⁺ ion	2	4	4	4	4	}	corresponds to
							A-atom.
" " " F ⁻ "	2	4	4			}	corresponds to
							Ne-atom.

This is the reason why the electrons in dielectric substance retain the stable equilibrium positions. They are displaced only a little by the external electric field. On the contrary, in metallic substances all atoms in ionic states constituting crystal have no corresponding charge to their valencies. Thus, the parts of the electrons departed from the mother atom will be free electrons. I think this is the chief difference in metal and dielectric.

In conclusion, I wish to express my sincere thanks to Prof. K. Terazawa, whose kind interest and valuable advise have been a source of inspiration for me in this work, and also I wish to express my gratitude to Prof. H. Nagaoka, and Prof. T. Terada for their kind suggestions and advices during the course of this work.

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抄 錄

結晶集合物質の熱膨脹係數に就て

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航空機材料研究の目的は色々あるでせうけれども、「與へられた或材料を航空機の如何なる箇所に如何に利用するが適當か」と云ふことと、これの逆で「これこれの用途に對して充分なるものを作るにはどうするか」と云ふ事が最も重要なものであると思はれます。

それで是等の研究を充分に推し進めますためには少くとも一つの方法として分子物理學的に各物質の内部構造を深く省察することが必要であつて、その結果その物理的諸性質と内部構造の關係及びその諸性質同志の間に存在する關係を明かにすることが出来れば上述の目的を達する上に大變役に立つことゝ考へられます。

この小論文では上の方針で進みますために先づ結晶集合物質の熱膨脹係數が溫度に對して如何に變るかといふことを最近の物質構造觀の上から論じて見たのであります。

無機有機を問はず多くの物質は結晶からなります。單一の結晶よりなるものもありますが多くは結晶の集合體です。近時 X 線の研究に依つてこれらの結晶が原子的に規則正しい空間格子配列をなすところの構造をもつことが明かになつて來ました。ところが一方に於ては是等の原子間に働く力及びその安定平衡に對する問題が獨逸の「ホルン」「ランデ」等の人々によつて盛に研究されました。その結果その力は電氣的であることが明瞭になり且つ又この力は化學的親和性をあらはす力と同じ性質であることや彈性、光及び熱に對する諸性質の根原をなすものであることもわかつたのであります。

それならば斯様な力でむすびついておる結晶集合體の溫度が上昇したならばどういふことが起るかといふに「アインシュタイン」が初めて唱導したやうに各原子がそれぞれ自己固有な振動をなして全體としての「エネルギー」配布の状態が「プランク」の量子論で考へられる法則に順ふことは明かなことであります。

この二つの事を基礎として

- (1) それに「クリュンアイゼン」の計算を加味して熱膨脹係數を導出して見ますとそれが分子力、原子的空間格子距離、原子配列に關する「マードルンク」常數及び常壓比熱と或關係式で結びつけられることがわかりました。

その式をまづ二原子結晶體について考へ、「ハロゲン」鹽類に應用して膨脹係數を實驗と比較し可なりよく一致することを見ました。更に進んでこれらの鹽類が絶對零度から常溫又は融解點までにどのくらい膨脹するものかの割合をしらべました。

それから螢石に應用して各原子の荷電が電子の二倍づゝであることを確めました。

(2) 更に一原子結晶に對する式を導き曾て「デバイ」が結晶體を彈性的連續體として導いた式と比較し兩者がよく一致することを見ました。

そして立方晶系に屬する (I) 面中心立方空間格子配列 (II) 體中心立方空間格子配列 (III) 「ダイヤモンド」型空間格子配列をなす固體元素物體の熱膨脹係數を算出して實驗と比較し「マードルンク」常數が各配列に對してよく一致することを見ました。

(3) 溫度に對する該係數の變化を「アルミニウム」「銅」の二つについて計算し實驗と比較しました。

(4) 上述の考察から「ホール」の電子的原子構造觀より觀て金屬と非金屬物質の構造の差違をいくらか深く見ることが出来ると思ひます。