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Effect of Temperature on the Intensity of X-Rays Scattered by Powdered Sodium Fluoride

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The ratio of the integrated intensities of a number of regularly reflected x-ray lines from powdered sodium fluoride crystals at room and liquid air temperatures has been studied by means of a photographic method. The results of the experiments show that the ratio varies with the angle as predicted by the Debye-Waller formula. The characteristic temperature of sodium fluoride was found to be equal to 442°K. This value agrees as well as one could expect with values calculated by the Lindemann melting-point formula and the known characteristic temperatures of sodium chloride or potassium chloride crystals. Using the known structure factor of sodium fluoride atoms at room temperature and assuming zero-point or no zero-point energy the structure factors of the atoms at rest have been calculated. A comparison with the theoretical structure factors of sodium fluoride and neon (sodium fluoride atoms are neon-like) and with the known experimental structure factor of gaseous neon atoms indicates that the assumption of zero-point energy is correct. The square root of the mean square amplitude of thermal vibration of the sodium and fluorine ions at room temperature was found to be equal to 0.182A.

THE first theoretical investigation of the effect of temperature on the intensity of x-rays reflected from simple cubic crystals composed of atoms of one kind was made by Debye.[1] He showed that if f is the structure factor of the atoms at rest, the structure factor F at any temperature T is

$$F=fe^{-M/2}, \tag{1}$$

where

$$M=\frac{6h^2}{mkT_c}\left\{\frac{\varphi(x)}{x}+\frac{1}{4}\right\}\frac{\sin^2\theta}{\lambda^2} \tag{2}$$

or

$$M=\frac{6h^2}{mkT_c}\cdot\frac{\varphi(x)}{x}\cdot\frac{\sin^2\theta}{\lambda^2},$$

according as one assumes zero-point energy of $\frac{1}{2}$ quantum per degree of freedom or no zero-point energy. Here h is Planck's constant, m is the mass of the atom, k is the gas constant, T_c is the characteristic temperature of the substance, $x=T_c/T$, $\varphi(x)$ is a function of x which function Debye evaluates in his paper, θ is one-half of the angle of deviation and λ is the wave-length of the incident radiation.

The above formula having been found to be in qualitative but not quantitative agreement, Waller[2] extended the theoretical study of this subject and modified Debye's formula to read

$$F=fe^{-M}. \tag{3}$$

This equation can be tested experimentally, except as regards zero-point energy, by measuring the ratio of the integrated intensity of any regularly reflected line at a temperature T_0 and the integrated intensity at various other temperatures T_1, for from Eqs. (2) and (3), noting that the integrated intensity ρ is proportional to F^2,

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[1] P. Debye, Verh. deutsch Phys. Ges. **15**, 678 (1913).

[2] I. Waller, Zeits. f. Physik **17**, 398 (1923).

we obtain,

$$\log (F/f)^2 = -2M, \tag{4}$$

whence

$$\frac{\lambda^2}{\sin^2 \theta} \log \frac{\rho_1}{\rho_0} = \frac{12h^2}{mkT_c} \left\{ \frac{\varphi(x_0)}{x_0} - \frac{\varphi(x_1)}{x_1} \right\}, \tag{5}$$

where ρ_1/ρ_0 is the ratio of the integrated intensities of a regularly reflected line at temperatures T_0 and T_1. It is assumed that the angle θ is the same for a line at all temperatures, which, of course is only approximately true. The left-hand side of Eq. (5) can be evaluated experimentally while the right-hand side can be calculated.

In experiments of this kind performed by James and Firth,[3] James and Brindley[4] and James, Brindley and Wood,[5] with single crystals of sodium chloride, potassium chloride or aluminum, and a temperature range that extended from liquid air to 900°K, agreement was found between theory and experiment up to about 400°K. At higher temperatures the experimental values dropped off more quickly than the calculated ones. They attributed this disagreement at higher temperatures to the fact that the assumptions in the theory lose validity at these elevated temperatures.

Even if the characteristic temperature of the crystal is not known, the Debye-Waller formula can still be experimentally tested. For two given temperatures the right-hand side of Eq. (5) is independent of λ and θ. Whether the left-hand side actually remains constant can be experimentally tested. If a constant is obtained, one can determine the characteristic temperature of the crystal by solving Eq. (5) for T_c. This being done one can, except as far as the assumptions of zero-point energy are concerned, test the formula completely.

In order to find a somewhat approximate value of T_c for the sake of comparison one can make use of Lindemann's melting-point formula[6]

$$(k/h)T_c = \nu = C(T_m/AV^{\frac{2}{3}})^{\frac{1}{2}} \tag{6}$$

where ν is the characteristic frequency, C is a known constant, T_m is the melting point temperature, A is the atomic weight and V is the specific volume of the crystal. From Eq. (5) one obtains,

$$T_c = (A'T_mV'^{\frac{2}{3}}/AT_m'V^{\frac{2}{3}})^{\frac{1}{2}}T_c', \tag{7}$$

where the unprimed quantities refer to the crystal in question and the primed quantities refer to the crystals whose characteristic temperatures are known.

One can therefore calculate the characteristic temperature of a crystal in terms of known characteristic temperatures of other crystals. This equation gives results which are only approximately correct, especially when one uses room temperature volumes, as can easily be seen when one actually calculates the characteristic temperature of one crystal in terms of others.

Waller[7] has shown that the temperature effect can be expressed in terms of the amplitude of vibration of the atoms. He obtains the equation

$$M = (8/3)\pi^2\overline{u_1^2}(\sin^2 \theta)/\lambda^2, \tag{8}$$

where $\overline{u_1^2}$ is the mean square displacement of the atoms at a temperature T_1. With the aid of this equation one can calculate the square root of the mean square amplitude of thermal vibration of the atoms at any temperature provided one knows whether or not zero-point energy exists.

To determine experimentally whether or not zero-point energy exists, one must know the magnitude of the temperature effect and the structure factors of the atoms at rest and at some other temperature.

Since the atoms of a monatomic gas are supposed to scatter independently of each other, therefore, as if at rest, f could be determined by placing the substance into the gaseous state. F, and the temperature effect, would, naturally, be determined when the substance were in the crystalline state. Though theoretically possible, experimentally it is very difficult to do this, since one can hardly find a substance which could be satisfactorily worked with in both the gaseous and solid states.

An alternative method is to calculate the value of f from some theory of atomic structure, and compare this calculated value with the experi-

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[3] R. W. James and E. Firth, Proc. Roy. Soc. **A117**, 62 (1927).

[4] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

[5] R. W. James, G. W. Brindley and R. G. Wood, Proc. Roy. Soc. **A125**, 401 (1929).

[6] W. Nerst und F. A. Lindemann, Zeits. f. Electrochemie **17**, 817 (1911).

[7] I. Waller and R. W. James, Proc. Roy. Soc. **A117**, 214 (1927).

mental value of F as measured from the crystal. This method, which has been applied by James and Brindley[4] and others,[8] is however subject to the criticism that the theoretical structure factors are known to be only approximate. A more direct comparison is obtained if we choose a crystal such as sodium fluoride, which is composed of neon-like atoms, and determine the structure factor f of the corresponding gaseous atoms.

A similar comparison of the reflection from chlorine ions in the sodium chloride crystal with the scattering by argon gas has been made in a preliminary way by Compton,[9] with data from various sources, and more carefully by Wollan with his own data for the scattering by argon[10] and those of James and Firth[3] for the reflection by the sodium chloride crystal.

The experiments about to be described were undertaken primarily to obtain evidence regarding the existence of a zero-point energy. For this purpose measurements were made of the effect of temperature on the integrated reflection from powdered crystals of sodium fluoride. Using existing data[11] for the reflection by this crystal at room temperature enables one to calculate the structure factor of sodium fluoride atoms at rest according as zero-point energy is or is not assumed.

The structure factor thus determined should correspond closely to the experimental structure factor determined by the scattering of x-rays from neon gas,[10] since the average of the sodium and fluorine ions should closely resemble the neon atom. A similar correspondence should exist between the theoretical structure factors of these substances. It will be shown by a comparison of the theoretical with the experimental curves that the same correspondence exists between the experimental as between the theoretical curves only when zero-point energy is assumed.

The comparison of sodium fluoride and neon has the advantage over that between other combinations insofar as, due to its low atomic weight and high characteristic temperature, the zero-point energy plays a more prominent part in the motion of its atoms. The present experiments have the further advantage that, since the measurements have been made with powdered crystals, difficulties due to extinction are avoided.

Because of the work that has already been done by other experimenters on other crystals over a wide range of temperatures, the author of this paper considered it sufficient to make measurements at room and liquid air temperatures only.

Apparatus and Procedure

The source of x-rays was a coolidge, water-cooled, oil-immersed x-ray tube having a molybdenum target. The rest of the apparatus except for slits and a film-holder was contained in a large hard-rubber cylinder C, 5 inches in diameter and 24 inches high, shown partly in section in Fig. 1. Enclosed within this cylinder and held firmly in place by wooden rings R rested the liquid-air flask F measuring $2\frac{3}{4}$ inches in diameter and 11 inches in depth. A heavy brass

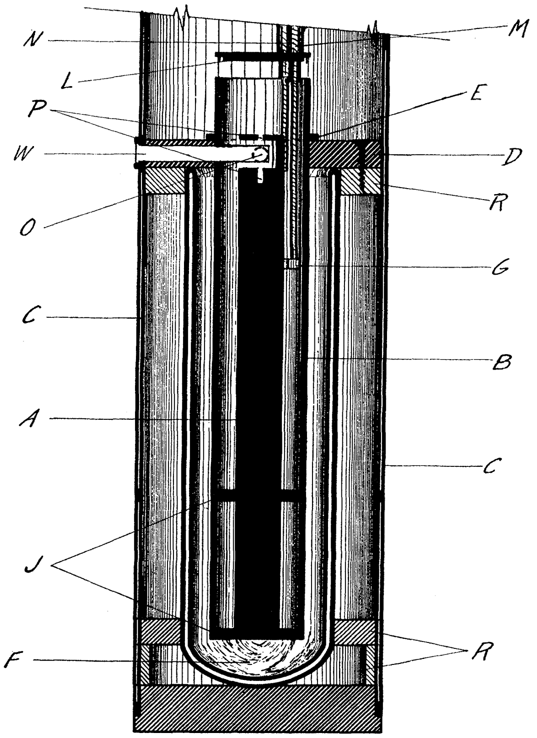

Fig. 1. Part-section of apparatus.

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[8] E. O. Wollan, Rev. Mod. Phys. **4**, 205 (1932). This paper contains an excellent summary of the work on the effect of temperature on the motion of atoms in a crystal

[9] A. H. Compton, Tech. Rev. **33**, No. 1, 19 (1930).

[10] E. O. Wollan, Phys. Rev. **37**, 862 (1931).

[11] R. J. Havighurst, Phys. Rev. **28**, 869 (1926).

cylinder *B*, 2 inches in diameter and 12 inches long, supported by means of a brass collar *E* on the wooden ring *D* which in turn rested on the flask *F*, extended well down to the bottom of the flask. A solid brass rod *A*, 1 inch in diameter, ran down the center of this cylinder and was held firmly in place by two perforated brass disks *J*. The axis of this rod coincided with the axes of the brass and hard-rubber cylinders. A slot was cut into the rod at right angles to its axis so that the powdered crystals, which were pressed into small thin glass tubes sealed at both ends, when placed in position *P*, came into thermal contact with the brass rod both above and below the x-ray beam. Thus the powdered crystals were surrounded, except for the apertures at *O* and *W*, by heavy brass walls which were immersed throughout the greater part of their length in liquid air. Openings were cut through the hard-rubber cylinder, the wooden ring *D*, and the brass cylinder at *O* and at *W*, *O* being a small hole through which the primary beam passed to the crystal and *W* a wide angular window at right angles to *O* through which the scattered rays came forth. Both *O* and *W* were sealed with celluloid which was kept dry quite easily during the winter months by means of a stream of air. The wooden rings *R* and *D* were made to fit snugly into the hard-rubber cylinder *C*, the space above, below, and around the flask was filled with felt, and the ends of the outside container *C* were sealed air-tight so that the whole was quite rigid and compact.

Two small hard-rubber tubes *M* and *N* passing through the brass lid *L* were the only external openings the apparatus had. *M* carried the buoy, liquid-air level indicator *G*, and *N* was used for adding liquid air and for introducing a thermocouple for measuring the temperature. Liquid air was added at intervals of one hour and a half, since the level dropped off at the rate of about 2 inches per hour.

The photographic film was held in a brass frame on the outside of the hard-rubber cylinder opposite the window *W* so that the film was always at room temperature. The film was wide enough so that both the liquid air and room temperature pictures were taken on it side by side. Exposures varied from a few hours to about thirty-eight hours.

The integrated intensity corresponding to the various lines on the film was determined by a method similar to that used by Froman,[12] except that a new photoelectric photometer constructed and described by Dershem was used.[13]

A line at room temperature was found to have the same shape as at liquid air temperature, as one would expect, so that it was only necessary to take the average of ten readings 0.002 cm apart over the maximum of the lines. The width of the photometer slit was 0.002 cm and its height was sometimes 0.3 and sometimes 0.5 cm.

It has been the experience of persons employing the photographic method in their work and using the above-mentioned photometer to make the measurements, that because of the great reliability of the instrument, the degree of reproducibility of results is high. Errors arising from non-uniformity of the emulsion on the film and from development were small since the lines to be compared were close together. Furthermore, it is probable that the errors caused by motion of the focal spot, thermal variation of the length of the target rod and variation in the line voltage averaged themselves out during the long exposures.

Quantitative measurements of the ratio of the integrated intensities of a line at liquid-air and room temperatures were not made for lines at small angles. No satisfaction could be expected from such measurements since the ratio is so nearly equal to unity at these small angles that a reasonably small error in its measurement would introduce a rather large error into the calculated quantity $(\lambda^2/\sin^2\theta)\log(\rho_2/\rho_1)$.

Measurements at large angles were not made either since at large angles the intensities are very small and very long exposures are necessary. To make measurements at large angles one would rather use the single crystal method. This method had however already been used by other experimenters on other crystals, and therefore it was considered unnecessary to make these measurements on sodium fluoride, especially since one needs to know only the number $(\lambda^2/\sin^2\theta)\log(\rho_2/\rho_1)$ which is independent of the angle, in order to determine the characteristic temperature

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[12] D. K. Froman, Phys. Rev. **36**, 1330 (1930).

[13] E. Dershem, Rev. Sci. Inst. **3**, 43 (1932).

of the crystal and to discuss the validity of the assumption of zero-point energy.

EXPERIMENTAL RESULTS

The sodium fluoride crystal was considered as being a simple cubic crystal composed of atoms of one kind of atomic weight 21 and atomic number 10. This assumption is nearly satisfied in sodium fluoride since the Na^+ and F^- ions have 10 electrons each and their atomic weights and numbers are nearly equal.

The results of the measurements on the two final films are given in Table I. The ratio of the integrated intensity at liquid air temperature to the integrated intensity at room temperature is represented by ρ_2/ρ_1. With the powdered crystals first at room temperature (295°K) and later at liquid air temperature (86°K), exposures were made on the one film for 24 hours and 20 hours, respectively, and on the other for 30 hours and 27 hours, respectively.

TABLE I. *Temperature effect.*

Reflection index	$\frac{\sin\theta}{\lambda}$	$\frac{\rho_2}{\rho_1}$	$\frac{\lambda^2}{\sin^2\theta}\log\frac{\rho_2}{\rho_1}$
420	0.484	1.249	0.947
422	0.531	1.349	1.059
440	0.612	1.434	0.957
600	0.650	1.531	0.993
620	0.684	1.566	0.956
622	0.718	1.635	0.949
		Average	0.976±0.012

These data indicate no variation in the quantity $(\lambda^2/\sin^2\theta)\log(\rho_2/\rho_1)$ greater than the probable error of the experiments.

Upon solving the equation

$$\frac{12h^2}{mkT_c}\left\{\frac{\varphi(x_1)}{x_1}-\frac{\varphi(x_2)}{x_2}\right\}=0.976 \tag{9}$$

for T_c one obtains

$$T_c=442°\text{K}. \tag{10}$$

The value of T_c could not be found in physical tables so that it has probably never been determined by other experimental methods. T_c calculated by Eq. (6) in terms of the known characteristic temperature of sodium chloride is equal to 436°K and in terms of the characteristic temperature of potassium chloride is equal to 454°K. These calculations show that a value of 442°K for T_c of sodium fluoride is certainly reasonable.

In Table II, are given the structure factors of the atoms at rest, calculated by Eq. (3) for the cases of both no zero-point and of zero-point energy. The values of the structure factor F at room temperature are those of R. J. Havighurst.[11] The value of M from Eq. (2) is $0.871\sin^2\theta/\lambda^2$ or $0.512\sin^2\theta/\lambda^2$ according as zero-point or no zero-point energy is assumed.

TABLE II. *Experimental values of structure factors of sodium fluoride.*

Reflection index	$\frac{\sin\theta}{\lambda}$	F room temp.	f no *z-p-e*	f *z-p-e*
200	0.217	7.12	7.29	7.42
220	0.306	5.40	5.66	5.86
311	0.360	4.42	4.62	4.98
222	0.375	4.19	4.50	4.73
400	0.433	3.29	3.62	3.87
331	0.471	2.86	3.26	3.47
420	0.4845	2.75	3.10	3.37
422	0.531	2.37	2.73	3.03
511	0.562	2.12	2.49	2.79
440	0.613	1.73	2.10	2.39
531	0.640	1.55	1.91	2.22
600	0.650	1.52	1.89	2.20
620	0.687	1.28	1.63	1.92
622	0.718	1.19	1.55	1.87
642	0.810	0.93	1.30	1.65
731	0.831	0.87	1.26	1.59
820	0.892	0.71	1.06	1.42
822	0.918	0.67	1.00	1.39
840	0.970	0.61	0.99	1.37
842	0.995	0.52	0.84	1.22

Average theoretical structure factor values of sodium fluoride atoms were taken from the individual values for sodium and fluorine ions as calculated by James and Brindley[14] according to Hartree's method of self-consistent fields. These values and also the theoretical structure factor values of neon as similarly calculated[14] are given in Table III. The experimental structure factor values of neon as determined by E. O. Wollan[10] are also given.

All values of Tables II and III are shown graphically in Figs. 2 and 3. A glance at Fig. 2 suggests that the curve which passes through the points representing the values of f when zero-

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[14] R. W. James and G. W. Brindley, Phil. Mag. **12**, 81 (1931).

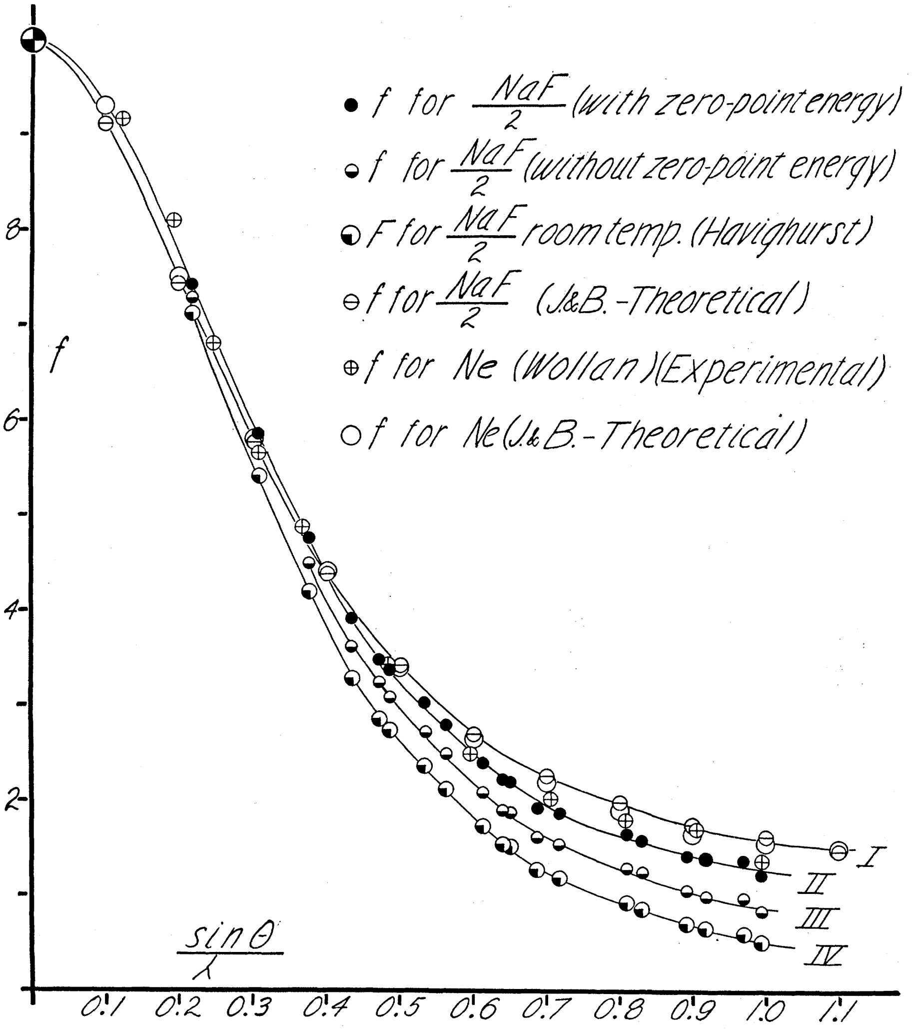

FIG. 2. Curve I, theoretical f(NaF); curve II, experimental f(NaF) with zero-point energy; curve III, f(NaF) without zero-point energy; curve IV, F(NaF) room temperature.

TABLE III. *Theoretical structure factor values of sodium fluoride and neon, and experimental structure factor values of neon.*

$\frac{\sin\theta}{\lambda}$	f(NaF) theory	f(Ne) theory	$\frac{\sin\theta}{\lambda}$	f(Ne) exp.
0.000	10.00	10.00	0.000	——
0.100	9.10	9.30	0.123	9.16
0.200	7.45	7.50	0.190	8.08
0.300	5.75	5.80	0.245	6.80
0.400	4.38	4.40	0.306	5.64
0.500	3.42	3.40	0.365	4.86
0.600	2.70	2.65	0.482	3.43
0.700	2.27	2.20	0.596	2.49
0.800	1.98	1.90	0.704	2.02
0.900	1.75	1.65	0.808	1.80
1.000	1.62	1.55	0.905	1.70
1.100	1.48	1.50	0.995	1.37

point energy is assumed should be given first consideration.

The curves representing the theoretical values of the structure factors of sodium fluoride and neon, the experimental values of the structure factor of neon and the structure factor values of sodium fluoride when zero-point energy is assumed are reproduced in Fig. 3. The experimental values are displaced through one unit in the negative direction of the structure factor axis in order to enable one to study the curves more easily and in greater detail.

An analysis of the theoretical curve shows that the structure factor values of sodium fluoride are

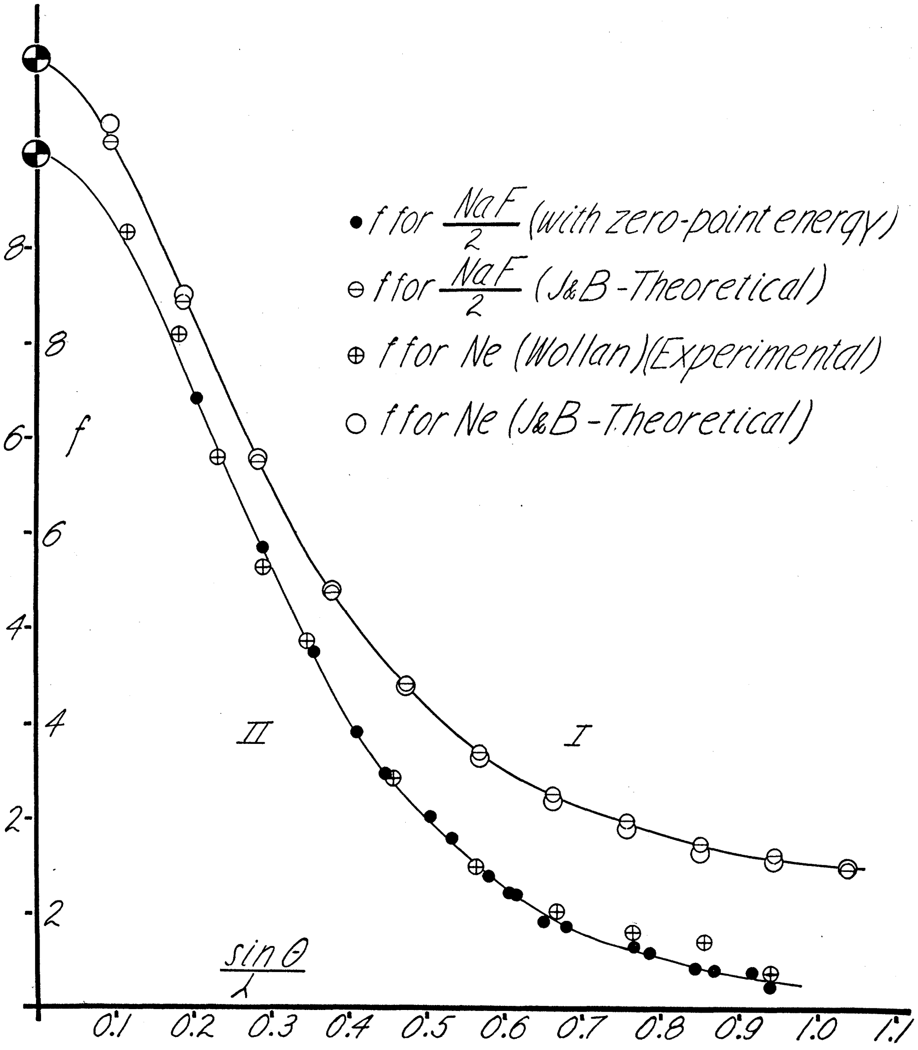

FIG. 3. Curve I, theoretical f(NaF); curve II, experimental f(NaF) with zero-point energy, shifted one unit in the negative direction of the structure factor axis.

slightly smaller than that of neon at small angles, slightly larger at larger angles and about equal at intermediate angles. The experimental curve, when corrected for zero-point energy, discloses similar characteristics, except that at large angles the neon values fall above the sodium fluoride values. This, however, can have nothing to do with the effect of the thermal motions, since it can be accounted for in terms of experimental errors.

A further study of the curves in Figs. 2 and 3 brings out the fact that the difference between the structure factors of neon and sodium fluoride, when no zero-point energy is assumed, is greater than the experimental error. When, however, zero-point energy is assumed, the crystal experiments are consistent with the gas experiments.

The square roots of the mean square amplitude of thermal vibration of the sodium fluoride atoms at any temperature can now be determined by Eq. (8). At room temperature

$$(\overline{u^2})^{\frac{1}{2}} = (3/8)0.871\pi^2 = 0.182\text{A}. \qquad (11)$$

CONCLUSION

The above data give further proof of the correctness of the Debye-Waller formula for the temperature effect and more conclusive evidence that the assumption of zero-point energy is correct. They also furnish us with the structure factor of sodium fluoride atoms at rest. Incidentally they provide us with a value of T_c of sodium fluoride crystals and the magnitude of the thermal displacements of these atoms.

It is interesting to note that no definite conclusions could have been drawn by studying the relation between the theoretical and experimental structure factor curves of sodium fluoride alone. It might also be mentioned that the theoretical structure factor values of both sodium fluoride and neon are apparently too small at the small angles and too large at the large angles.

In conclusion, the author wishes to express his appreciation to Professor A. H. Compton, under whose direction this work has been done, as also to E. Wollan and E. Dershem for their suggestions and continued assistance during the working of this problem.