

AN X-RAY INVESTIGATION OF THE LAMBDA POINT AND A  
DETERMINATION OF THE DEBYE-WALLER FACTOR IN  
POTASSIUM BOROHYDRIDE

by

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ABSTRACT

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The nature of the lambda point transition in potassium borohydride at 76 degrees Kelvin was investigated by measuring the X-ray diffraction patterns of powder samples above and below the transition temperature. The low temperature powder patterns were measured at liquid helium temperatures. The structure was found to be a face-centered cubic sodium chloride structure both above and below the transition. The mechanism of similar lambda points in other compounds having tetrahedral ions is discussed.

The Debye-Waller temperature factor for potassium borohydride was determined by comparing experimental values of structure factors with structure factors calculated from atomic scattering factors without including temperature dependent terms. At 300 degrees Kelvin the values of the angle and wavelength independent part of the Debye-Waller factor were found to be  $0.44 \text{ \AA}^2$  for potassium and  $11.7 \text{ \AA}^2$  for boron. These values correspond to Debye characteristic temperatures of 165 degrees Kelvin for boron and 484 degrees Kelvin for potassium.

Thesis Supervisor: B.L. Averbach  
Professor of Metallurgy

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## I. INTRODUCTION

### A. Lambda Point Transitions Involving Tetrahedral Ions.

It has been observed that many ionic crystals in which one ion is geometrically a tetrahedron undergo gradual transitions of the lambda point type. Lambda points have been observed in the ammonium halides (1), in which the ammonium ion is tetrahedral, and the alkali borohydrides (2) with the borohydride having a tetrahedral configuration as shown in Figure 1. A gradual transition of the lambda point type manifests itself in a specific heat curve as shown in Figure 2.

Pauling (5) initially postulated that the transitions in the ammonium halides are a consequence of the onset of rotational freedom for the ammonium ion tetrahedra. Frenkel (6) however, postulated that the lambda point arises from a change in the degree of order in the orientation of the tetrahedra, and that no rotational freedom is attained on passing through the transition. There are two essential differences between the Pauling model, in which the ions are rotating, and the disordered state of the Frenkel model. First the two are energetically different. The energy associated with the Pauling model is that of free rotation, while the energy associated with the Frenkel model is that of oscillations. The second difference has to do with the average position of the vertices of the tetrahedra. In the Pauling model, the distribution of the vertices is uniform over the surface of a sphere of radius equal to the bond length associated with a tetrahedron and centered on the

center atom of the tetrahedron. In the Frenkel model, the positions of the vertices are averaged over the allowable tetrahedral orientations, and in general the distribution will be non-spherical. It is possible to choose between these two mechanisms by examining the infra-red spectrum and specific heat curves of the crystals, and, more directly, by determining the neutron diffraction patterns of the crystal above and below the transition temperature.

It has been shown by Lawson (7) that the observed specific heat curve for ammonium chloride is not compatible with Pauling's rotation mechanism. The value of the specific heat at constant volume at a temperature just above the transition is 18 calories per mole per degree, of which 12 calories per mole per degree may be attributed to the normal lattice vibrations. The remaining 6 calories per mole per degree are associated with the behavior of the ammonium ion tetrahedra. If the assumption of free rotations of the tetrahedra is made, a value of 3 calories per mole per degree is obtained. If, however, one adopts the Frenkel model of order in the orientations of the tetrahedra below the transition but not above, allowing the existence of oscillations but not free rotations, the correct contribution to the heat capacity is obtained.

Further support for the Frenkel mechanism is obtained from the infra-red spectrum of ammonium chloride. Wagner and Hornig (1) report no evidence of a rotational spectrum either above or below the transition temperature. In addition, a torsional oscillation has been identified

at a frequency much higher than a possible rotational frequency. This torsional oscillation removes all of the degrees of freedom which might be available to rotation.

Neutron diffraction provides a means to unambiguously decide between the two conflicting mechanisms, since by its use the hydrogen atom positions may be determined. The results of Levy and Peterson (8,9) for ammonium chloride and ammonium bromide indicate the Frenkel mechanism to be the correct one.

It is instructive to examine the order-disorder mechanism in more detail. In ammonium chloride the nitrogen and chlorine atoms are arranged in a cesium chloride structure (7). In order to lower the electrostatic energy, the nitrogen-hydrogen bonds are directed toward the chlorine nearest neighbors of the nitrogen atoms. There are two equivalent ways in which this may be done, as shown in Figure 3. Below the transition temperature all of the tetrahedra are in one of the two positions with all tetrahedra parallel. Above the transition temperature, the two positions are occupied at random. The transition in ammonium bromide (8) is slightly more complicated. The ordered phase of ammonium bromide is tetragonal, but may be considered as a distortion of the cesium chloride structure with alternate strings of ammonium ions in an antiparallel position. A summary of the transitions in the ammonium halides and the deuterio-ammonium halides is given in Table 1.

The alkali borohydrides, with the exception of lithium borohydride, have lambda point transitions similar to the ammonium halides (2). Only the transition in sodium borohydride has been investigated in

any detail (2,3,10). There is a considerable amount of evidence indicating that the transition in sodium borohydride is of the Frenkel order-disorder type as in the ammonium halides. There is no evidence in the infra-red spectrum (11) of any rotational freedom of the borohydride ion, and the specific heat curve (3) is not compatible with any rotational freedom. This precludes the Pauling explanation for the transition.

Positive evidence for the Frenkel mechanism is the value of the excess entropy of transition, 1.2 calories per mole per degree (2). This approximately equal to  $R \ln 2$ , the value to be expected from a two equivalent position order-disorder transition.

Above the transition temperature, the sodium and boron atoms are arranged in a sodium chloride structure (10). Since the orientation of the hydrogen atoms is not revealed by x-ray diffraction and since no neutron diffraction investigation has been done, the tetrahedral orientations must be inferred from more indirect evidence, such as by analogy to Phase I of the ammonium halides which has a sodium chloride structure.

With the sodium chloride structure there is no possible way that the tetrahedral hydrogen atoms can all make a simultaneous minimum approach to the octahedrally distributed nearest neighbor atoms, a halide ion in the ammonium halides or a sodium ion in sodium borohydride. This consideration leads to three possible types of orientations being available to the tetrahedral ion. In the first case the ion may undergo free or nearly free rotation. Secondly, the tetrahedral ion may be so oriented that only one hydrogen atom makes a minimum approach to the nearest neighbor atom. In the third case the orientation of the tetrahedra may

be such that the hydrogen atoms lie on cube diagonals, and the hydrogen bond is in the direction of second nearest neighbors. There is evidence that the second configuration is the correct one in Phase I of ammonium iodide and ammonium bromide (12, 13, 14). This configuration allows one-dimensional rotation, and therefore cannot be the correct one for sodium borohydride.

The third type of orientation must be the correct one for sodium borohydride, since, in addition to allowing no rotational freedom, there are two equivalent tetrahedral orientations, as shown in Figure 4, which is consistent with the observed excess entropy of transition,  $R \ln 2$ .

It has been postulated by Stockmayer and Stephenson (2) that in the ordered phase the tetrahedra in alternate (200.) planes are arranged in an antiparallel orientation, similar to the ordered tetragonal phase of ammonium bromide, Phase III. This will increase the average hydrogen pair separation, each member of the pair being in different ions, and will lower the energy of hydrogen-hydrogen repulsion. The energy of repulsion can be further lowered by a distortion of the unit cell from cubic to tetragonal. This distortion has been observed by x-ray analysis (10).

Potassium borohydride has a lambda-point transition at 76 degrees Kelvin (4, 15, 16). A comparison of the specific heat curves of potassium borohydride and sodium borohydride, Figure 2, shows that the lambda point of potassium borohydride is much sharper than that of sodium borohydride. In addition, the specific heat curve of potassium borohydride has an inflection point at 190 degrees Kelvin and rises anomalously higher than the curve for sodium borohydride. Because of the sharpness of the lambda

point and the fact that the excess entropy of transition, 0.7 calories per mole per degree, is less than  $R \ln 2$ , it was postulated by Stephenson (17) that the transition might be from the sodium chloride structure to a cesium chloride structure, analagous to the Phase I-Phase II transition in the ammonium halides. Until this time there had been no investigation of the crystal structure of potassium borohydride below the transition temperature so the validity of this postulate was not known.

B. The Debye-Waller Temperature Factor.

The total intensity of crystal monochromated x-rays diffracted by a given set of hkl planes in a powder sample is given by (18):

$$I = K(F_{hkl})^2 \left( \frac{1 + \cos^2 2\theta_m \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)_{hkl} \quad I-1$$

where:

- $m_{hkl}$  = multiplicity of hkl planes
- $\theta$  = Bragg angle of sample
- $\theta_m$  = Bragg angle of crystal monochromator
- $K$  = constant which depends on the intensity of the x-ray beam incident on the sample, the efficiency of the detecting system, and the absorption by the specimen, but is independent of the scattering angle.

$$F_{hkl} = \text{structure factor of the hkl planes}$$

The structure factor is given by:

$$F_{hkl} = \sum_{n=1}^N f_n e^{2\pi i(hu_n + kv_n + lw_n)} \quad I-2$$

where:

$f_n$  = the atomic scattering factor of the n th atom

$u_n, v_n, w_n$  = the coordinates in the unit cell of the n th atom

and the summation extends over all atoms in the unit cell.

The atomic scattering factor,  $f$ , is a measure of the efficiency of an atom for scattering x-rays and is a function of the scattering angle. Values of  $f$  are calculated from the radial distribution of electric charge density of an atom at rest. The effect of thermal motion is to smear the electric charge density to a larger radii and therefore change the atomic scattering factor to a value given by (19):

$$f = f_0 e^{-M} \quad \text{I-3}$$

The factor,  $M$ , known as the Debye-Waller temperature factor is given by:

$$M = 8\pi^2 \overline{u^2} \left( \frac{\sin\theta}{\lambda} \right)^2 \quad \text{I-4}$$

where:

$\overline{u^2}$  = the mean square displacement of the atom from its mean lattice position, measured at right angles to the reflecting planes.

$\lambda$  = x-ray length

The structure factor,  $F_{hkl}$ , corrected for the temperature effect is now given by:

$$F_{hkl} = \sum^n f_{on} e^{-M_n} e^{2\pi i(hu_n + kv_n + lw_n)} \quad \text{I-5}$$

The Debye-Waller factor will be dependent on the temperature and increases as the mean square displacements increase with temperature.

A detailed theory has been developed for the case of a simple cubic crystal containing one kind of atom. In this case the temperature dependence of  $M$  is given by (20):

$$M = \frac{6h^2T}{mk^{\Theta}2} \left\{ \bar{\Phi}(x) + \frac{x}{4} \right\} \frac{\sin^2\theta}{\lambda^2} \quad \text{I-6}$$

where:

$$\begin{aligned} h &= \text{Planck's constant} \\ k &= \text{Boltzmann constant} \\ m &= \text{mass of the atom.} \\ T &= \text{absolute temperature} \\ \Theta &= \text{Debye characteristic temperature} \\ x &= \frac{\Theta}{T} \\ \bar{\Phi}(x) &= \frac{1}{x} \int_0^x \frac{xdx}{e^x - 1} \end{aligned}$$

Although equation I-6 is strictly good only for simple cubic crystals of one kind of atom, its use has been extended to face-centered and body-centered cubic crystals with more than one kind of atom with some success (20).

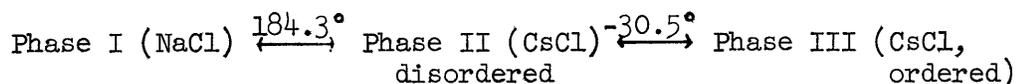
The Debye-Waller factor may be determined experimentally by measuring the variation with temperature of the integrated intensity of Bragg peaks, measuring the diffuse scattering caused by the existence of temperature vibrations, or by comparing measured structure factors with structure factors calculated from atomic scattering factors with no correction for the effect of temperature. Prior to this investigation no measurements of the Debye-Waller factor for potassium borohydride had been made.

TABLE I

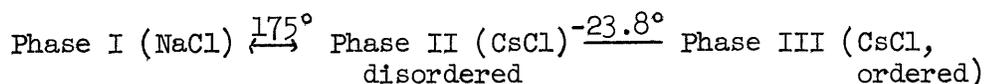
A SUMMARY OF THE PHASE TRANSITIONS IN THE  
AMMONIUM AND DEUTERO-AMMONIUM HALIDES<sup>(9)</sup>

The notation in the parentheses indicates the structure of the phase. All transition temperatures are in degrees Centigrade.

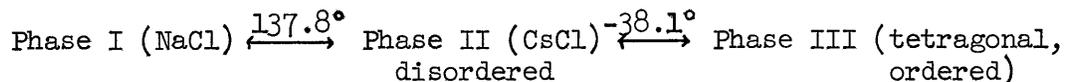
NH<sub>4</sub>Cl:



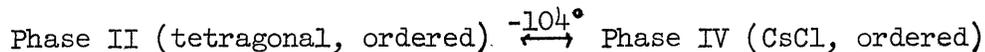
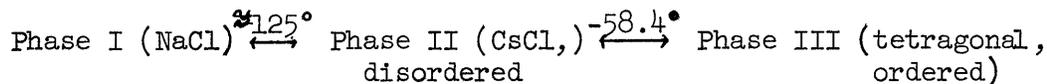
ND<sub>4</sub>Cl:



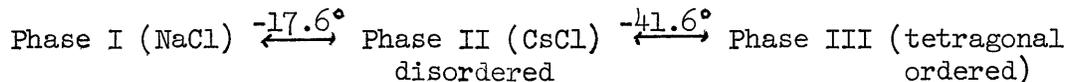
NH<sub>4</sub>Br:



ND<sub>4</sub>Br:



NH<sub>4</sub>I:



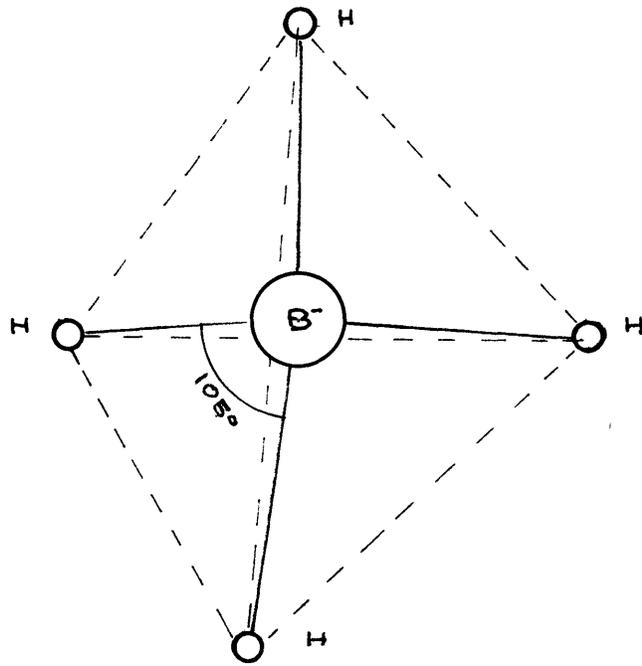


FIGURE 1. THE TETRAHEDRAL GEOMETRY OF THE  $\text{BH}_4^-$  ION.

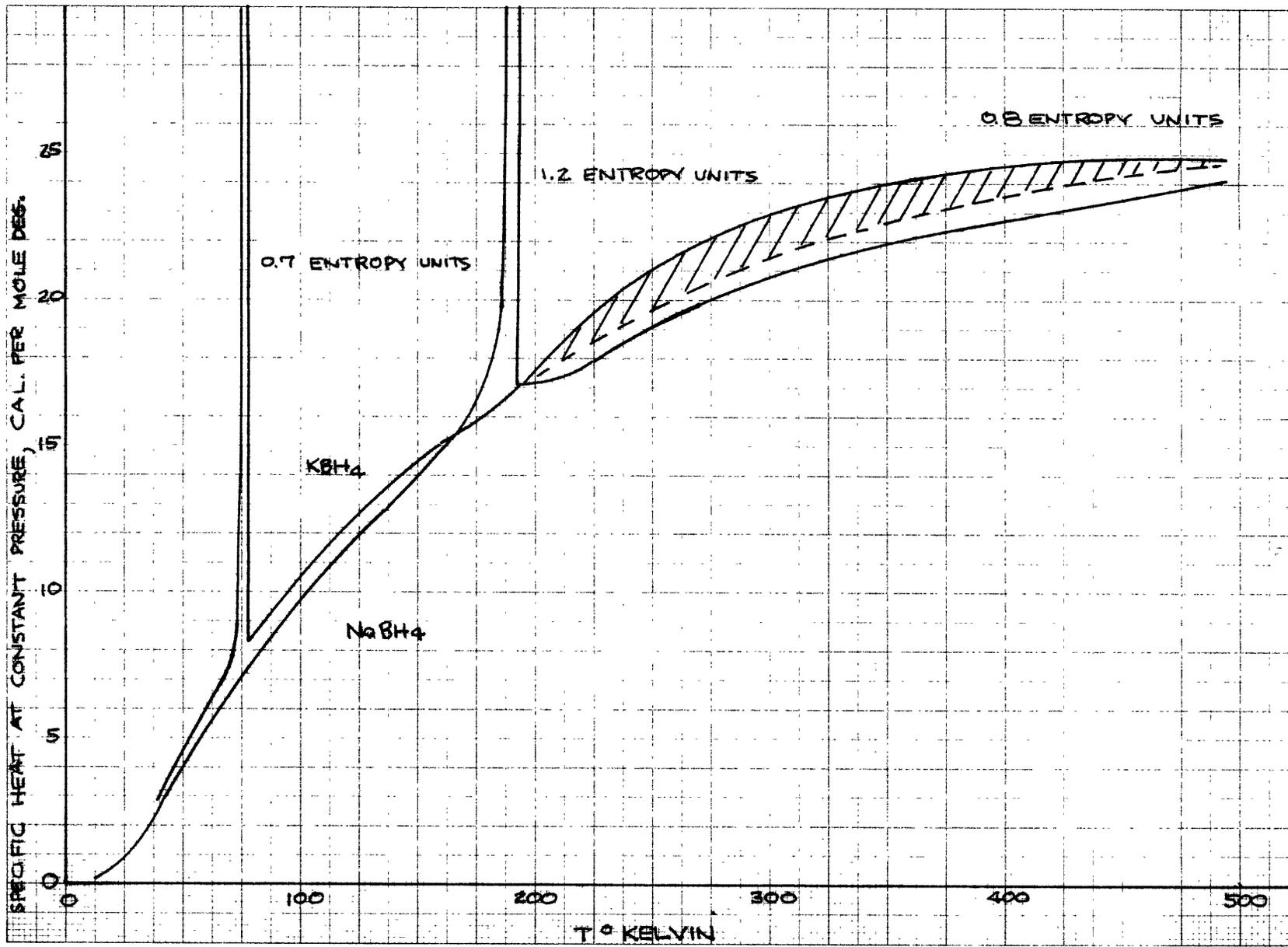


FIGURE 2. SPECIFIC HEAT CURVES FOR SODIUM BOROHYDRIDE<sup>(3)</sup> AND POTASSIUM BOROHYDRIDE<sup>(4)</sup>

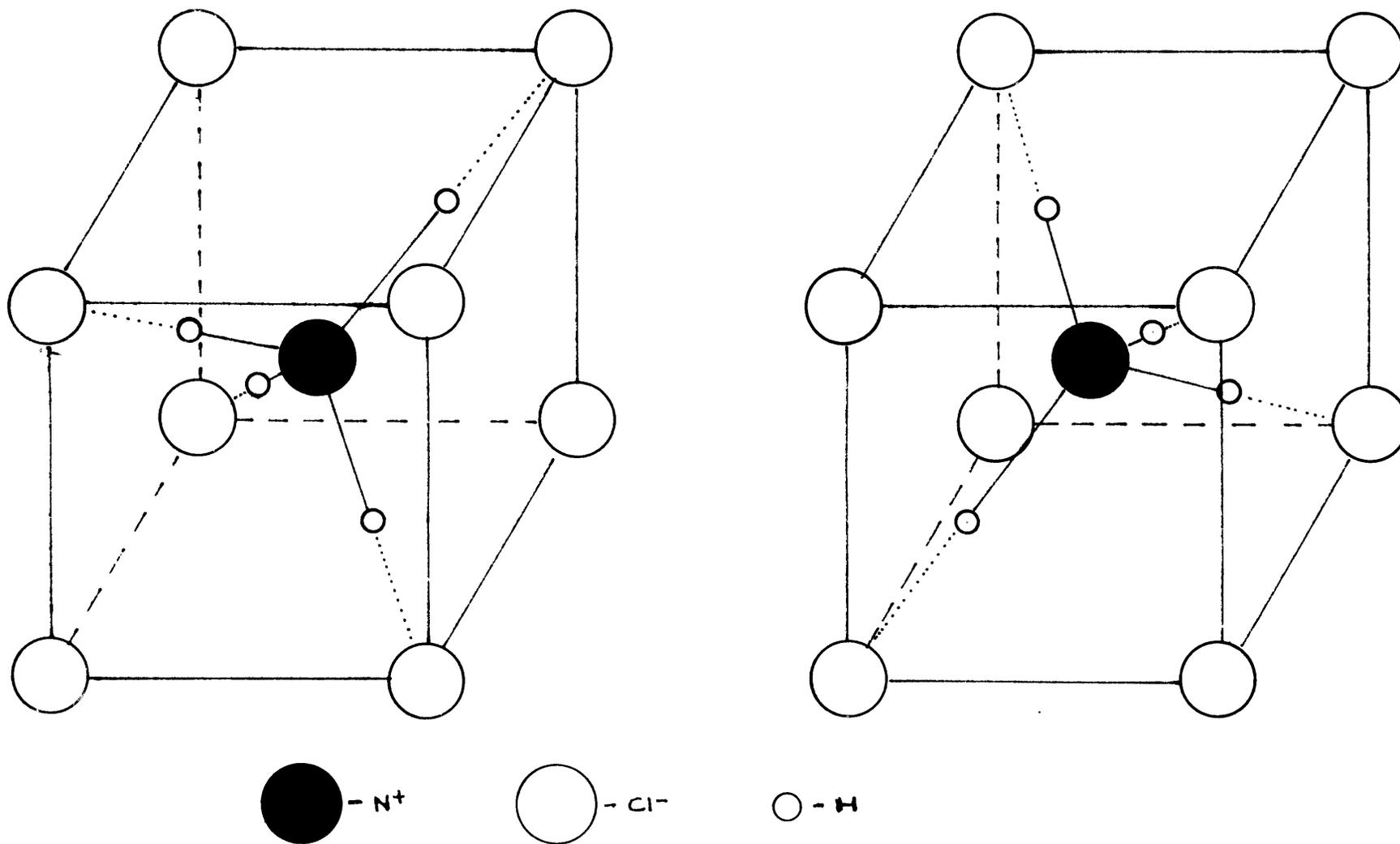


FIGURE 3. THE TWO EQUIVALENT ORIENTATIONS OF THE AMMONIUM ION IN A CESIUM CHLORIDE TYPE LATTICE.

TOP VIEW OF (200) PLANE WITH TETRAHEDRA  
RANDOMLY DISTRIBUTED BETWEEN POSITIONS  
1 AND 2.

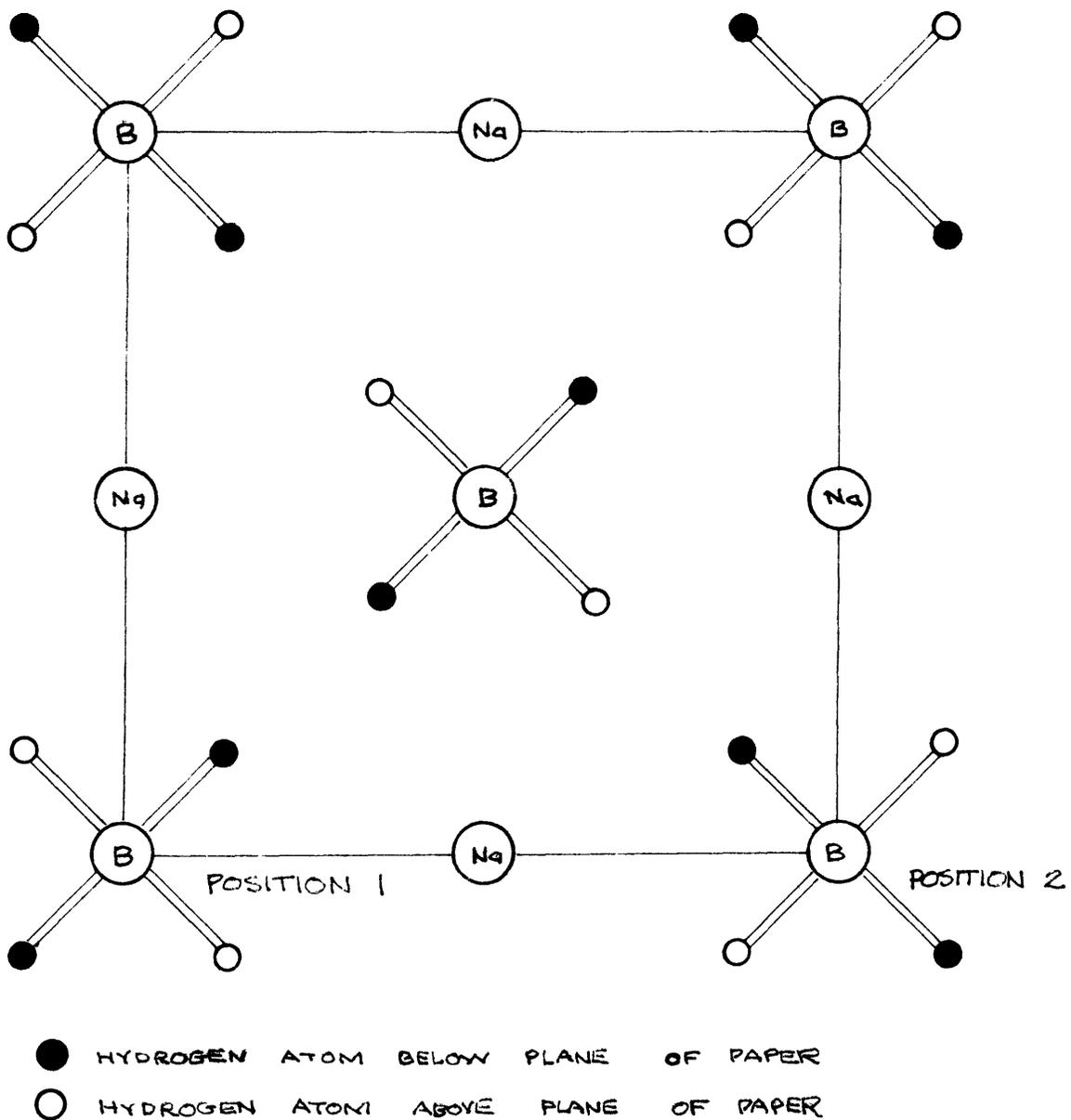


FIGURE 4. ORIENTATION OF BOROHYDRIDE TETRAHEDRA  
IN THE SODIUM CHLORIDE STRUCTURE OF SODIUM  
BOROHYDRIDE.

## II. OUTLINE OF INVESTIGATION

The purpose of the investigation was two-fold, to determine the crystal structure of potassium borohydride below its lambda point transition temperature, 76 degrees Kelvin, and to determine the Debye-Waller factor of potassium borohydride.

The first part of the problem consisted of cooling a sample below 76 degrees Kelvin and obtaining sufficient x-ray data to establish the correct crystal structure. This was done using a liquid helium cooled cryostat which served as a sample holder for an x-ray diffractometer, and with it obtaining powder sample diffractometer recordings at liquid helium temperatures.

The second part of the problem was attacked by measuring the integrated intensities of several Bragg peaks of powder samples of potassium borohydride at room temperature, calculating structure factors from these integrated intensities and comparing these experimental structure factors with structure factors calculated not including the Debye-Waller exponential term.

### III. DESCRIPTION OF EQUIPMENT

X-ray investigations were carried out using a motor-driven automatic diffractometer. The x-ray source was a line focus, copper target x-ray tube operated at 45 kilovolts and 16.5 milliamps. The x-rays were monochromated to the wavelength of copper  $K\alpha$ ,  $1.542 \text{ \AA}$ , by means of a singly-bent silicon crystal monochromator. The x-ray detection system consisted of a scintillation counter, pulse-height analyzer, scaler, and counting rate meter. The output of the counting rate meter was continuously recorded on a recording potentiometer. The x-ray tube, monochromator, slit system, sample, and scintillation counter were arranged in a parallel, double focussing geometry as shown in Figure 5.

Low temperatures were obtained using a liquid helium cryostat designed by H. Posen. A detailed description of this apparatus is forthcoming in another publication, therefore only a general description of this equipment will be given here. A schematic drawing of the cryostat is shown in Figure 6.

The cryostat consists of a cylindrical helium flask with a copper sample holder, one end of which is immersed in liquid helium and which serves as a conduction path between the helium bath and the sample. Surrounding the helium flask is a concentric cylindrical liquid nitrogen jacket. The entire jacket, flask, and sample holder assembly is contained in a cylindrical can which is evacuated with an oil diffusion pump. The entire cryostat is mounted on the center post of the diffractometer so that the sample is centered on the diffractometer axis. The x-rays pass

into and exit from the cryostat through an aluminized Mylar window. The temperature of the sample was monitored with a copper-constantin thermocouple placed against the specimen.

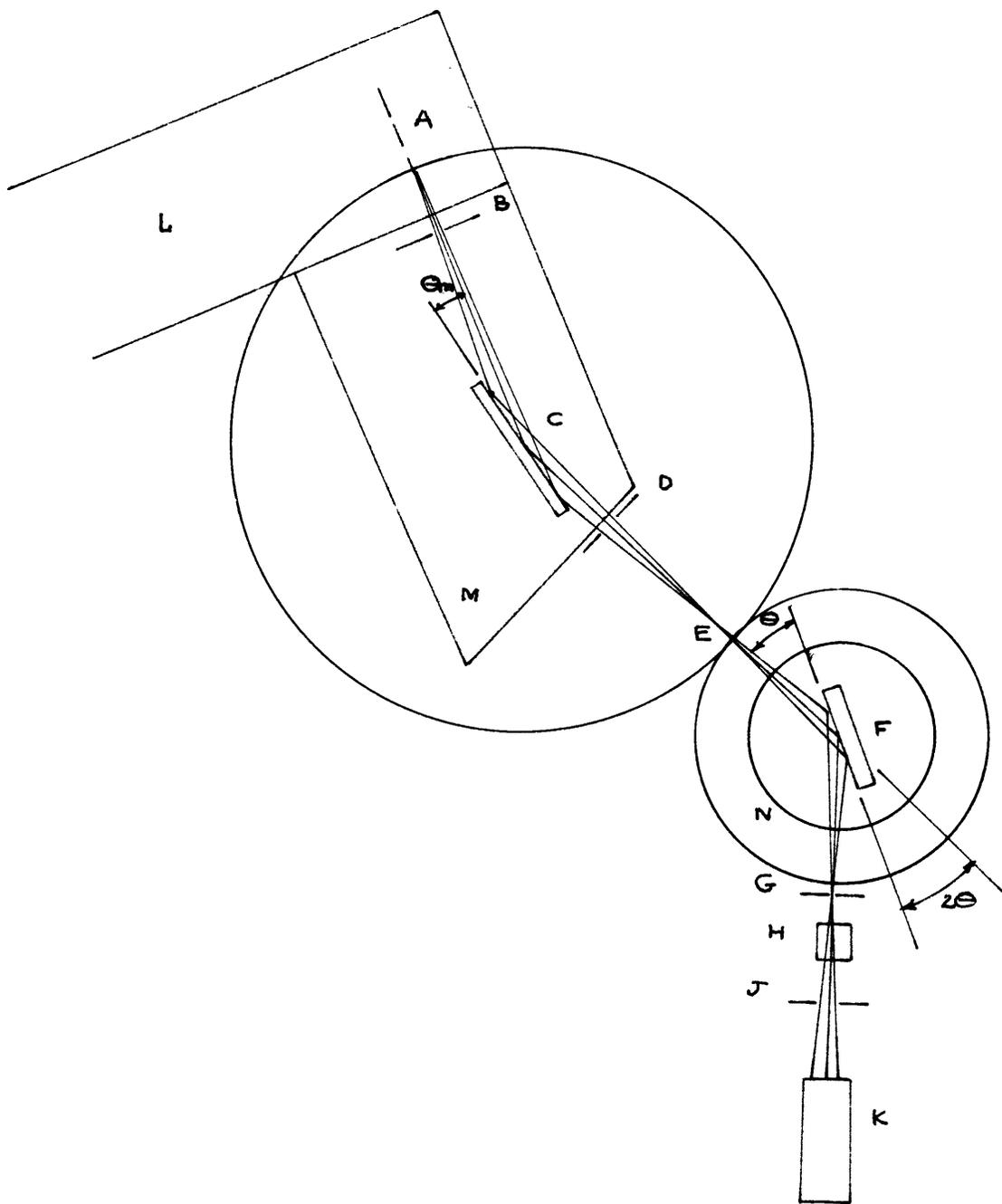


FIGURE 5. PARALLEL DOUBLE FOCUSING GEOMETRY OF  
DIFFRACTOMETER  
(LEGEND IN TABLE II.)

TABLE II

Legend for Figure 5

- A. X-Ray Line Focus
- B. Defining Slits
- C. Bent Silicon Monochromator
- D. Scatter Slits (Non-Defining)
- E. First Focus
- F. Specimen
- G. Receiving Slits, Second Focus
- H. Soller Slits, Vertical Divergence =  $4^\circ$
- J. Scatter Slits, (Non-Defining)
- K. Detector (Scintillation Counter)
- L. X-Ray Tube
- M. Monochromator Box
- N. Cryostat Window

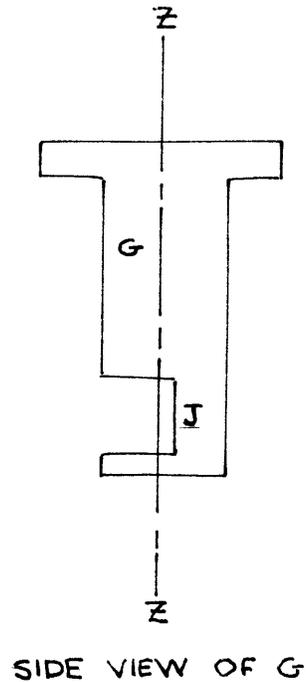
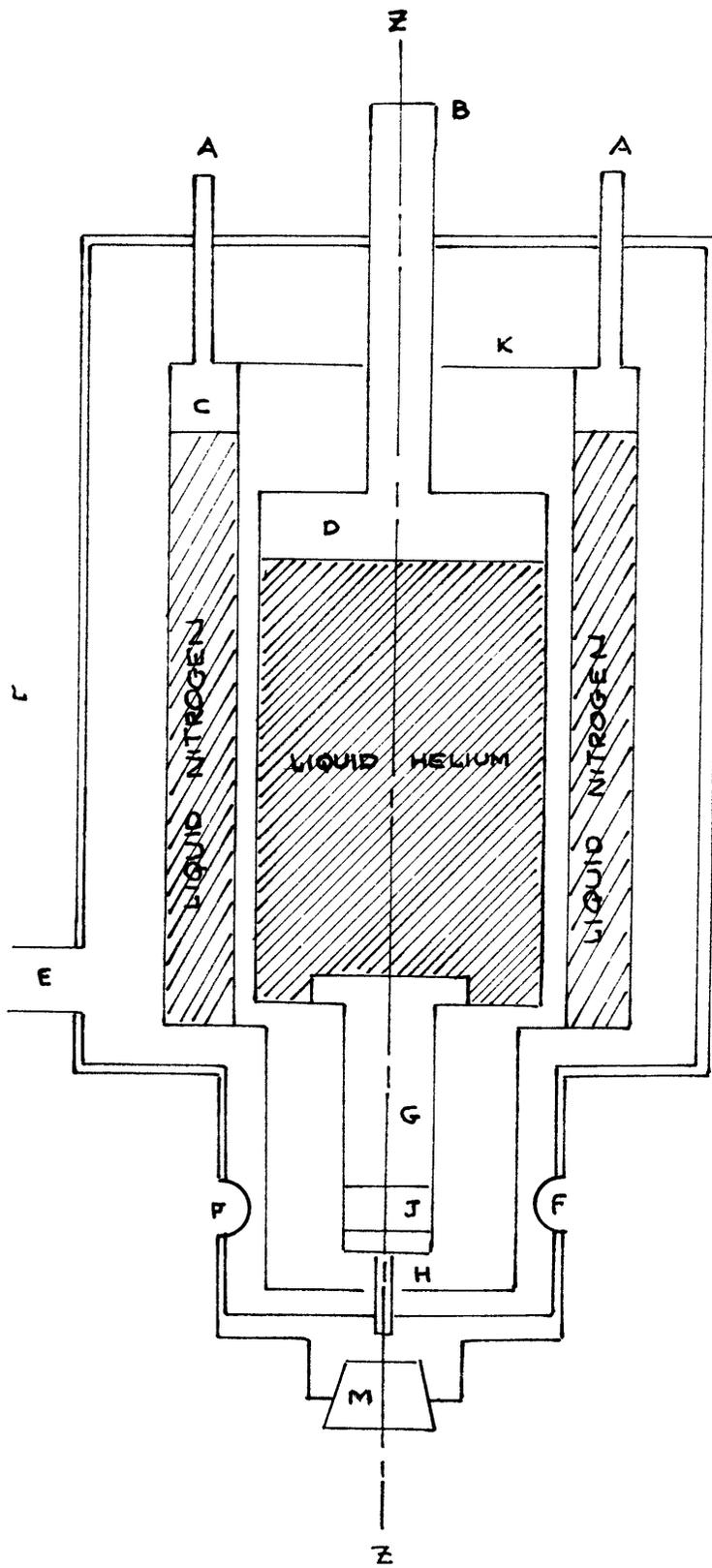


FIGURE 6. SCHEMATIC DRAWING OF CRYOSTAT  
LEGEND IN TABLE III

TABLE III

Legend for Figure 6

- A. Liquid Nitrogen Inlets
- B. Liquid Helium Inlet
- C. Liquid Nitrogen Jacket
- D. Helium Flask
- E. Port to Vacuum Pump
- F. Mylar Window to Admit X-Rays
- G. Copper Specimen-Holding Block
- H. Alumina Centering Pin
- J. Sample Briquette
- K. Aluminum Foil Radiation Shield
- L. Outside Can
- M. Diffractometer Center Post

#### IV. EXPERIMENTAL PROCEDURE

X-ray diffraction samples were prepared from commercial grade potassium borohydride and sodium borohydride crystals supplied by Metal Hydrides, Inc. The potassium borohydride was 98+% pure, and the sodium borohydride was 97+% pure. X-ray samples were made in the form of rectangular briquettes, 1 inch by 1/2 inch by approximately 1/16 inch. The samples were prepared by grinding the as-received powder in a mortar and pestle and pressing the ground powder into briquettes in a rectangular die at a pressure of 5000 pounds per square inch. The as-received material and prepared samples were stored at all times in a vacuum dessicator to prevent hydration, and exposure to air was kept to a minimum, because although potassium borohydride is stable in moist air, sodium borohydride readily forms a dihydrate (21). One sample each of potassium borohydride and sodium borohydride was annealed in a dynamic vacuum. The sodium borohydride sample was annealed for 4 hours at 120 degrees Centigrade. The potassium borohydride sample was annealed for 10 hours at 75 degrees Centigrade followed by 5 hours at 120 degrees Centigrade.

The investigation of the transition was carried out in the following manner. The sample was inserted in the cryostat and the first ten Bragg peaks, (111.) through (511,333.), were scanned at a rate sufficiently slow to establish the peak shape, generally 1/16 degree  $2\theta$  per minute. It was generally impossible to measure Bragg peaks at higher angles than the (511,333.) because the attenuation of the x-ray beam by the radiation shielding and the Mylar window of the cryostat resulted in the

diffracted intensity of the weak higher angle peaks being too low to measure with any accuracy.

Following the room temperature measurements, both the liquid nitrogen jacket and the liquid helium flask of the cryostat were filled with liquid nitrogen, and when a constant temperature was established the Bragg peaks were again scanned in the same manner as was done at room temperature. During a run the sample temperature remained constant within  $\pm 1$  degree Centigrade, as indicated by the copper-constantin thermocouple. Temperatures of different runs varied between 81 and 91 degrees Kelvin.

Two different methods were employed to cool the potassium borohydride samples below the transition temperature, 76 degrees Kelvin. The first method, used in preliminary experiments, was to keep the liquid helium flask filled with liquid nitrogen following the measurements at liquid nitrogen temperature, and to reduce the pressure in the flask by pumping on the flask filling-inlet using a mechanical vacuum pump. This lowered the boiling point of nitrogen sufficiently to maintain temperatures from 69 to 73 degrees Kelvin for periods of about one hour. During this time a diffractometer recording was made by scanning at a rate of 2 degrees  $2\theta$  per minute.

The second method was to use liquid helium to cool the sample. Following the liquid nitrogen run, the liquid nitrogen remaining in the flask was pumped out, and the flask was flushed out with flowing helium gas to remove any remaining gaseous nitrogen. Liquid helium was then introduced into the liquid helium flask. The equilibrium temperature

ranged between 15 and 25 degrees Kelvin and could be maintained for about 3 hours. After this time leaks would develop in the vacuum system and the runs would be terminated. The time at temperature was sufficiently long to make a rapid scan at 2 degrees  $2\theta$  per minute over the range of  $2\theta$  containing the first nine Bragg peaks and to make individual scans over the first five peaks at a rate of  $1/8$  degree  $2\theta$  per minute.

## V. EXPERIMENTAL RESULTS

### A. Transition

The room temperature structure was found to be that reported by Abrahams and Kalnajs (10), face-centered cubic with a sodium chloride structure. Since all measurements were made at low angles, no attempt was made to precisely determine the lattice parameter, but it did not appear to differ significantly from the value of Abrahams and Kalnajs, 6.727 Å. Similarly, the liquid nitrogen measurements revealed no change from the sodium chloride structure, as is to be expected since the transition takes place below the normal boiling point of liquid nitrogen. In Table IV, experimental values of the structure factor measured at 300 degrees Kelvin and 80 degrees Kelvin are compared with the structure factor calculated assuming a sodium chloride structure.

Two measurements were made utilizing pumping on liquid nitrogen to lower the sample temperature below the transition temperature. These measurements, at 69 and 73 degrees Kelvin, revealed no change from the sodium chloride structure.

When sodium borohydride is cooled below its transition temperature, 190 degrees Kelvin, the structure changes from the face-centered cubic sodium chloride structure to what may be considered a slightly tetragonal sodium chloride structure (10). The effect on the diffraction pattern is for each cubic line to split into three lines if  $h \neq k \neq l$ , to split into two lines if  $h \neq k = l$ , and to remain one line if  $h = k = l$ . A diffraction pattern of sodium borohydride was made at 80 degrees Kelvin to check the magnitude of

the line splitting which might be expected in potassium borohydride if the transition is the same. It was found that no change occurred in the structure of sodium borohydride unless the sample was previously annealed at 120 degrees for 4 hours before cooling below the transition. Using an annealed sample it was observed that the line splitting occurred by the time the cryostat had been filled with liquid nitrogen. The split lines had a separation, on the average, of about  $1\frac{1}{2}$  degrees  $2\theta$ , and the transformed structure was easily recognizable. The transition is reversible since on warming the sample to room temperature, the sodium chloride structure was again observed.

Two diffraction patterns were made for unannealed samples of potassium borohydride at 15 and 25 degrees Kelvin. The observed structure was the sodium chloride structure, as may be seen from Table IV, and there was no change in the peak shapes from those observed at room temperature. A sample of potassium borohydride was annealed for 10 hours at 75 degrees Centigrade and subsequently for 5 hours at 120 degrees Centigrade, and the diffraction pattern of this sample when cooled to liquid helium temperatures revealed no change from the sodium chloride structure and no change in peak shape.

#### B. Debye-Waller Factor

The room temperature data for the integrated intensities of the first nine Bragg peaks were used to determine the temperature factors for potassium and boron. The data were treated using the analysis derived in Appendix I. A plot of the experimental structure factors is shown in

Figure 7. Plots are given in Figures 8 and 9 of a linear function of  $\sin^2\theta/\lambda^2$  whose slope is the angle independent part of the Debye-Waller factor, B, where:

$$M = B \sin^2\theta/\lambda^2 \qquad \text{V-1}$$

The slopes of the straight lines in Figures 8 and 9 yield values of B of 0.44 Å for potassium and 11.7 Å for boron at 300 degrees Kelvin. These B values correspond to root mean square displacements, Equation I-4, of 0.075 Å for potassium and 0.384 Å for boron. If it is assumed that Equation I-6 holds for the case of face-centered cubic crystals with more than one kind of atom per unit cell, these B values correspond to Debye characteristic temperatures of 484 degrees Kelvin for potassium and 165 degrees for boron.

TABLE IV.

COMPARISON OF EXPERIMENTAL STRUCTURE FACTORS FOR  $\text{KBH}_4$   
WITH STRUCTURE FACTORS CALCULATED ASSUMING A  
SODIUM CHLORIDE STRUCTURE

<u>hkl</u>	<u>F<sub>calc.</sub></u>	<u>F<sub>300° K</sub></u>	<u>F<sub>82° K</sub></u>	<u>F<sub>15° K</sub></u>
111	1.13	1.01	1.00	1.17
200	1.97	2.08	2.10	2.00
220	1.70	1.67	1.80	1.90
311	0.93	0.94	1.15	1.10
222	1.51	1.34	1.50	1.60
400	1.37	1.00	1.40	1.40
331	0.80	0.74	0.85	
420	1.25	1.01	1.20	
422	1.18	0.84	1.20	
511,333	0.72	0.66	0.80	

All structure factors are in arbitrary units.

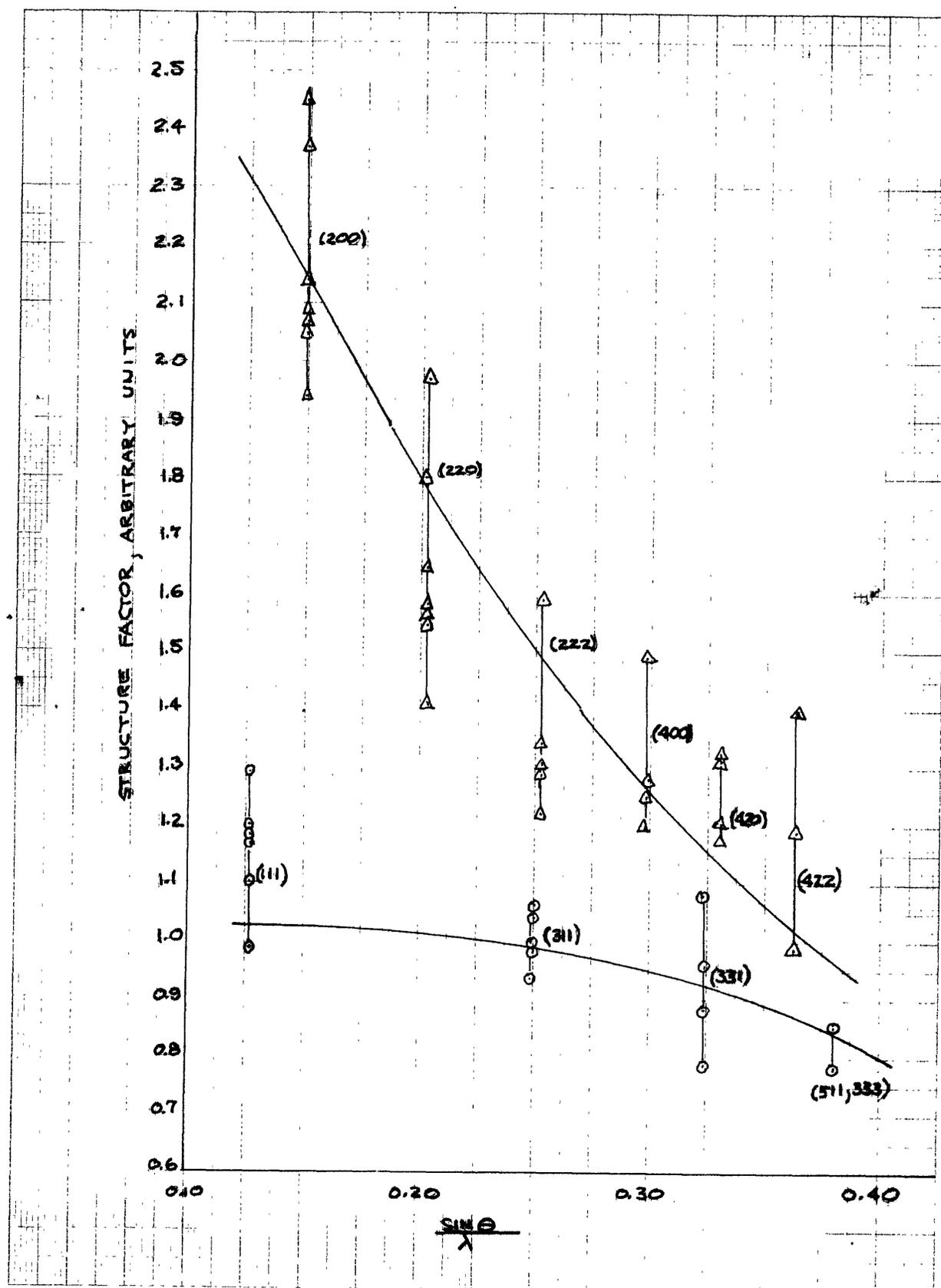


FIGURE 7. EXPERIMENTAL VALUES OF STRUCTURE FACTOR OF POTASSIUM BOROHYDRIDE AT 300°K.

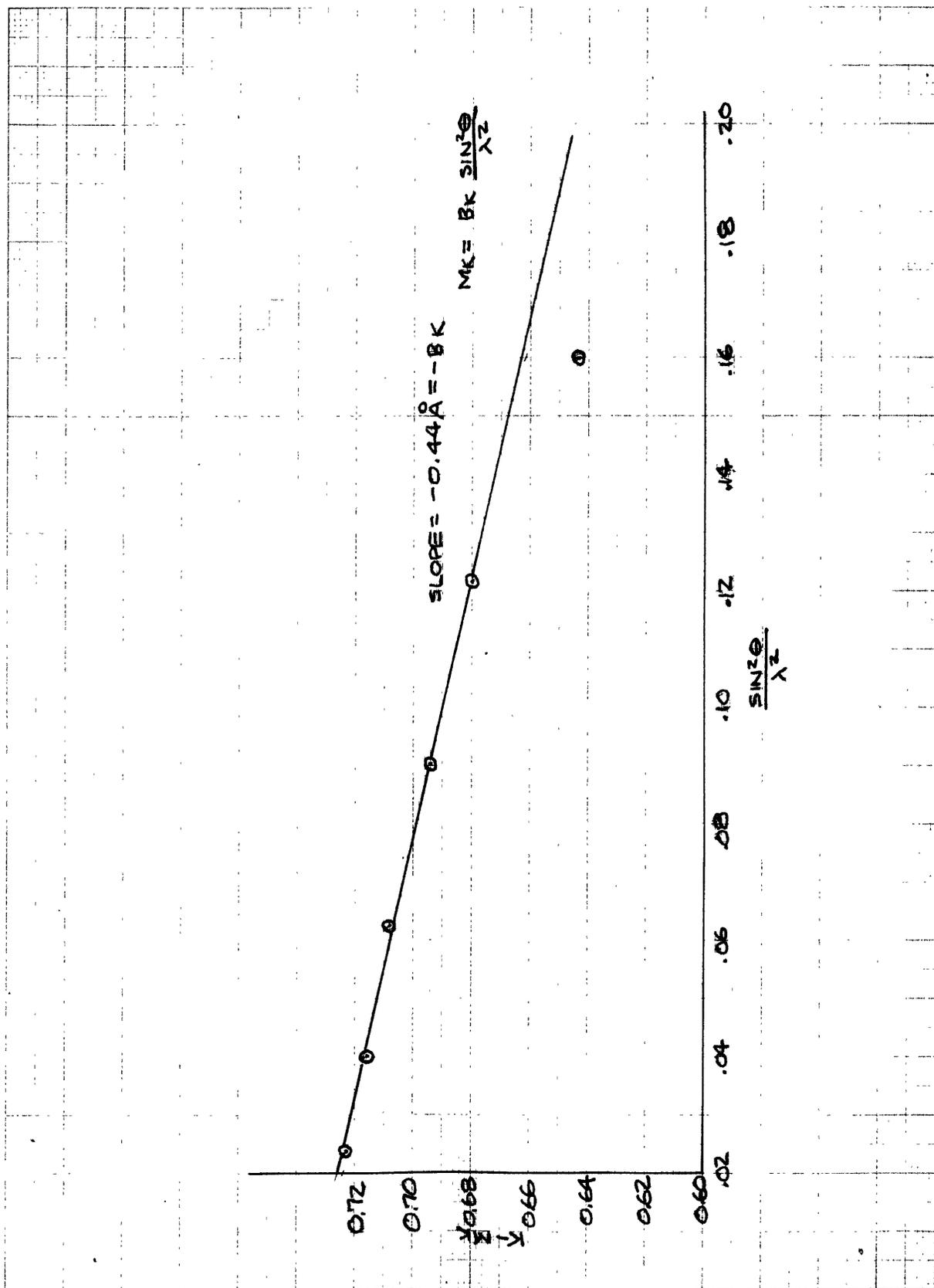


FIGURE 8. LINEAR FUNCTION OF DEBYE-WALLER FACTOR FOR POTASSIUM ION IN POTASSIUM BOROHYDRIDE AT 300°K.

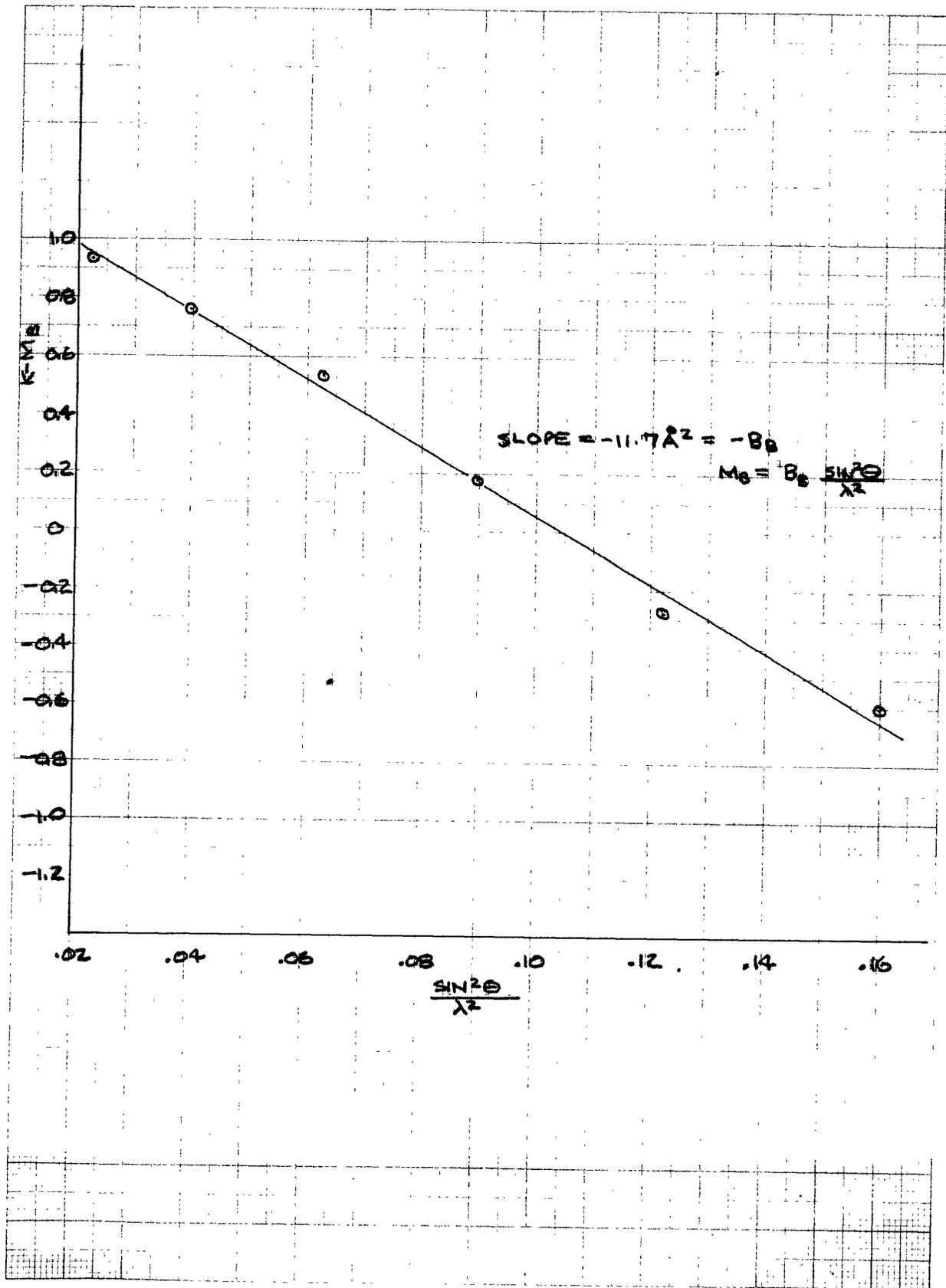


FIGURE 9. LINEAR FUNCTION OF DEBYE-WALLER FACTOR FOR BORON ION IN POTASSIUM BOROHYDRIDE AT 300°K.

VI. DISCUSSION OF RESULTS

It may be concluded that the structure of potassium borohydride both above and below the transition is such that the positions of the potassium and boron atoms are described by a face-centered cubic lattice and a sodium chloride structure. This is not consistent with the theory of Stephenson (17) that the transition is one from a sodium chloride to a cesium chloride structure. This result, however, does not clarify the nature of a possible transition involving a loss of order among the orientations of the borohydride tetrahedra and any hypothesis must be purely speculative. It is likely that the transition is of the order-disorder type observed in sodium borohydride, but that the tetragonality associated with the transition in sodium borohydride is absent in potassium borohydride because of the higher polarizability of the potassium ion, 1.00, than that for the sodium ion, 0.24 (22), and because the lattice parameter of potassium borohydride is larger than that of sodium borohydride making the hydrogen-hydrogen pair separation in neighboring borohydride ions smaller, hence making the overlap energy considerations less important. The fact that the observed entropy change associated with the transition, 0.7 calories per mole degree, is smaller than the expected value in such a transition,  $R \ln 2$ , may be the consequence of a short-range order among the orientations of the tetrahedra which persists to the higher temperatures. The occurrence of an anomaly in the specific heat curve between 200 and 500 degrees Kelvin supports this model. If the "normal" specific heat curve is extrapolated parallel to the specific heat

curve of sodium borohydride, as in Figure 2, and the excess entropy associated with the anomaly is calculated, the result is 0.8 calories per mole per degree. The sum of this entropy and that associated with the lambda point is 1.5 calories per mole degree or approximately  $R \ln 2$ .

The Debye-Waller factors for potassium and for boron calculated from the room temperature integrated intensities are quite different, as to be expected from the large difference in masses between the two ions, the B factor for boron being  $11.7 \text{ \AA}^2$  and that for potassium being  $0.44 \text{ \AA}^2$ . There is also a wide difference in Debye temperatures for the two ions, 484 degrees Kelvin for potassium and 165 degrees Kelvin for boron. Although there is no report in the literature of the Debye temperature of potassium borohydride, it should be comparable to that for sodium borohydride. The average of the two Debye temperatures mentioned above for potassium and boron is 324 degrees Kelvin, which is roughly comparable to the value reported for sodium borohydride, 268 degrees Kelvin (3).

Since there is no value available for the atomic scattering factor of the B- ion, the atomic scattering factor for carbon was used since the carbon atom has the same number of extranuclear electrons as B-. This will result in some error in the Debye-Waller factors. Another source of error is the assumption that the root mean square displacements have the same magnitude in all crystallographic directions. These errors are probably small compared to the error resulting from the large amount of scatter in the experimental structure factors, probably resulting from preferred orientation in the powder samples.

It may be concluded that the lattice positions of the potassium

and boron ions in potassium borohydride may be described as a face-centered cubic sodium chloride structure both above and below the transition temperature. It is likely that the transition is of the Frenkel order-disorder type with two equivalent orientations, and short range order may exist above the transition temperature. The Debye characteristic temperatures of the potassium and boron ions are 484 and 165 degrees Kelvin, respectively.

VII. SUGGESTIONS FOR FURTHER INVESTIGATION

1. The most important and definitive work that can be done to ascertain the exact nature of the lambda point transition is to perform neutron diffraction experiments. This will determine the change in orientation of the borohydride ions associated with the transition and determine the existence of short-range order above the transition temperature. In order for these experiments to be feasible, the potassium borohydride must be synthesized from the  $B_{11}$  isotope of boron since the absorption coefficient for thermal neutrons by natural boron is prohibitively high.
2. Precision lattice parameter measurements should be made just above and below the transition to determine any anomalous volume change associated with the transition.
3. A more accurate evaluation should be made of the Debye-Waller factor by utilizing:
  - a. spinning specimens to eliminate the effect of preferred orientation in the sample.
  - b. long time counting techniques to reduce statistical error.
4. The effect of crystallographic direction on the root mean square displacements should be determined by measuring the change with temperature of the intensity diffracted from different hkl planes.

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APPENDIX ICALCULATION OF DEBYE-WALLER FACTOR FROM X-RAYDIFFRACTOMETER RECORDINGS

The total intensity diffracted from a set of hkl planes in a powder sample is given by:

$$I = K_1 |F_{hkl}|^2 \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)^{m_{hkl}} \quad \text{A-1}$$

$$K_1 = \text{constant, independent of angle}$$

$$\left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)^m = \text{Lorentz-polarization factor, henceforth referred to as L.P.}$$

$$m_{hkl} = \text{multiplicity factor}$$

For potassium borohydride:

$$|F_{hkl}| = |(f_K e^{-m_K} \pm f_B e^{-m_B})| \quad \text{A-2}$$

The sign of  $\pm$  is positive when h, k, and l are all even and negative when h, k, and l are all odd, and the structure factor is zero when h, k, and l are mixed.

If a powder pattern is obtained as a continuous strip chart recording, the area, A, under a Bragg peak is a measure of the total diffracted intensity, hence by rearranging Equation A-1:

$$K_2 |(f_K e^{-m_K} \pm f_B e^{-m_B})| = \sqrt{\frac{A_{hkl}}{m_{hkl} \text{ L.P.}}} = |F| \quad \text{A-3}$$

If the function,  $|F|$  is plotted versus  $\sin \theta/\lambda$  a curve with two branches is obtained, as in Figure 7, where one branch,  $F_0$  is for

hkl odd and one branch,  $|F_E|$ , is for hkl even.

$$|F_E| = K_2 |f_K e^{-m_K} \pm f_B e^{-m_B}| \quad A-4$$

$$|F_O| = K_2 |f_K e^{-m_K} - f_B e^{-m_B}| \quad A-5$$

If Equation A-4 and Equation A-5 are added at a given value of  $\sin \theta/\lambda$ , a function involving only the Debye-Waller factor for potassium is obtained:

$$|F_E| + |F_O| = K_3 f_K e^{-m_K} \quad A-6$$

Similarly, by subtracting  $|F_O|$  from  $|F_E|$ :

$$|F_E| - |F_O| = K_3 f_B e^{-m_B} \quad A-7$$

By dividing Equations A-6 and A-7 by the appropriate atomic scattering factors and taking logarithms, a linear function of  $\sin^2 \theta/\lambda^2$  is obtained:

$$\ln \frac{|F_E| + |F_O|}{f_K} = K_4 - B_K \sin^2 \theta/\lambda^2 \quad A-8$$

$$\ln \frac{|F_E| - |F_O|}{f_B} = K_4 - B_B \sin^2 \theta/\lambda^2 \quad A-9$$

where:

$$m_K = B_K \sin^2 \theta/\lambda^2 \quad A-10$$

$$m_B = B_B \sin^2 \theta/\lambda^2 \quad A-11$$

Plotting the left-hand side of Equations A-8 and A-9 versus  $\sin^2 \theta/\lambda^2$  yields straight lines, the slopes of which are the angularly independent parts of the Debye-Waller factors.