The same procedure was followed in treating ammonia. Assuming a rigid symmetrical pyramid as the structure of the ammonia molecule, the rotational energy levels are given by the formula:

$$E = \frac{h^2}{8\pi^2}\left[\frac{j(j+1)}{A} + \left(\frac{1}{C} - \frac{1}{A}\right)T^2\right] \quad T \leqq j.$$

Defining $\sigma_1 = h^2/8\pi^2 A kT$

$$\sigma_1 = \frac{h^2}{8\pi^2 A kT} \quad \sigma_2 = \frac{h^2}{8\pi^2 kT}\left[\frac{1}{C} - \frac{1}{A}\right]$$

the rotational entropy, S_r, of the symmetrical top is

$$S_r = R\left[\ln Q - \sigma_1\frac{\partial \ln Q}{\partial \sigma_1} - \sigma_2\frac{\partial \ln Q}{\partial \sigma_2}\right].$$

According to Villars there are two varieties of ammonia, nuclear quartet and doublet, existing in equal amounts in ordinary ammonia.

For A, the moment of inertia perpendicular to the symmetry axis, (the one occurring twice), we use the value of Dickinson, Dillon and Rasetti (loc. cit.), 2.792×10^{-40} gram cm^2. For C, the moment of inertia around the symmetry axis, we use the value 3.49×10^{-40} gram cm^2 given by Badger (Phys. Rev. **35**, 1036 (1930)). With these constants in the two Q series of Villars, we obtain the following results for the rotational entropy at 298.1°:

$$^4S_r = 13.98 \qquad ^2S_r = 13.98.$$

Therefore $S_r\mathrm{NH_3} = 13.98 + R \ln 2 = 15.36$. With the same vibrational frequencies selected by Villars, we obtain 0.11 unit for the vibrational entropy at 298.1°. Villars calculated this to be 0.06, but made an arithmetical error. The Sackur-Tetrode translational en-

tropy is 34.45. Since the nitrogen nucleus has a spin of one unit, we must add to the quantities enumerated above, $R \ln 3$, to obtain the absolute entropy.

$$S_{\mathrm{NH_3}}^{298.1} = 34.45 + 15.36 + 0.11 + 2.18$$
$$= 52.10 \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

The difference between this value and that of Giauque, Blue and Overstreet is exactly accounted for by the difference in the amount assigned to vibrational entropy and by the difference in the value used for C in the two calculations. We wish to emphasize the fact that the value calculated from the Tetrode equation is in exact agreement with the above value if the same constants are used.

The absolute entropy of ammonia minus the limiting spin entropy is $52.10 - R \ln 24 = 45.79$. This is in good agreement with the experimental value 46.1, calculated by Giauque, Blue and Overstreet from the entropies of N_2 and H_2 and the free energy data of Lewis and Randall (Thermodynamics, p. 557).

The question as to whether the value 45.79. will be equal to that obtained for the entropy of ammonia by means of the third law of thermodynamics cannot be answered *a priori*. This will depend on the situation existing in the solid, and must be decided by experiment. Nevertheless, regardless of any complications such as rotation in the solid, and so forth, the value 45.79 is the one which should be used in thermodynamic calculations.

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Macroscopic and Lattice Expansion of Bi Single Crystals

J. K. Roberts[1] has been the first one to measure the thermal expansion coefficient of Bismuth single crystals normal ($\alpha_\perp$) and parallel ($\alpha_\parallel$) to the principal axis in the range between room temperature and melting point (272°C), in order to check the relation between specific heats (c) and the thermal expansion in anisotropic metal crystals proposed by Grüneisen and Goens.[2]

Roberts found an almost perfect constancy of $\alpha_\parallel$ and $\alpha_\perp$ for three Bi crystals between 30°C and 230°C. The values obtained in this region were: $\alpha_\perp = 12.0\times10^{-6}$ and $\alpha_\parallel = 16.2 \times10^{-6}$. Above 230°C however $\alpha_\parallel$ as well as

$\alpha_\perp$ decreased rapidly to almost one half of their value at 260°, i.e., still 10° below the melting point of the crystal. Since Robert's experiments prove the effect to be reversible one cannot ascribe it to a plastic deformation of the heated crystal caused by the weight of the measuring device.

In order to study this anomaly closer the expansion coefficient of the lattice was stud-

[1] J. K. Roberts, Proc. Roy. Soc. **A106**, 385 (1924).

[2] E. Grüneisen and E. Goens, Phys. Zeits. **24**, 506 (1923); Zeits. f. Physik **29**, 141 (1924).

ied by means of x-rays. A Bragg spectrometer of high accuracy was used, of which the detailed description will be published soon. The reflected intensities of a carefully selected bismuth crystal at the (111) plane were measured gives the mean of the observations of Roberts when these are translated to Bragg angles for the 5th order reflection of $K\alpha \mathrm{Mo} = 0.708\mathrm{A}$ with the known lattice spacing of the (111) plane ($D = 3.945\mathrm{A}^3$ at 23°C). The circles give
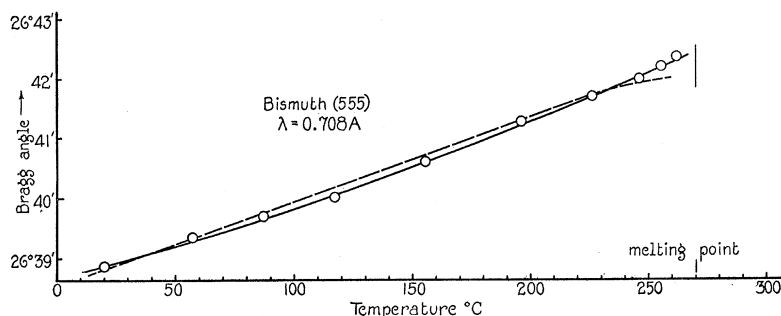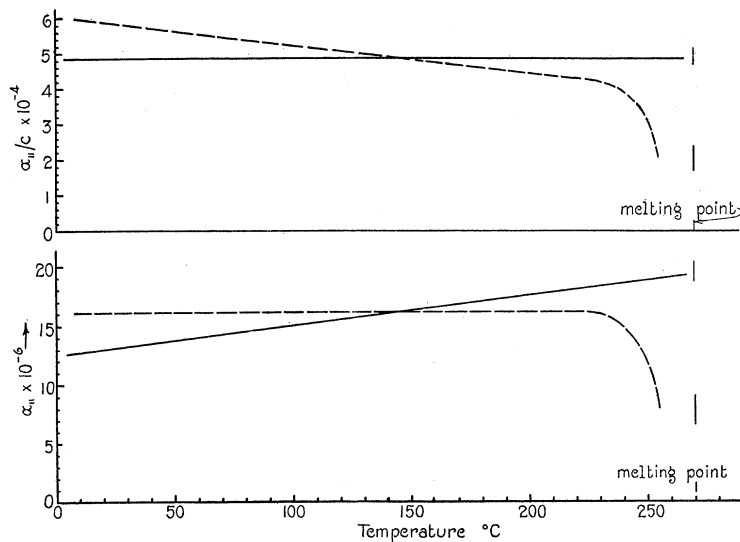

Fig. 1.

as a function of temperature, with an ionization chamber of special design and a Hoffmann electrometer. By these means it was possible to obtain an accuracy of the thermal expansion of the same order as the macroscopic observations, and it thus has been possible to decide whether or not the "decay" of our data obtained from the position of the intensity maximum of the Bragg-reflexions from the (111) plane of MoKα-radiation in the fifth order at different temperatures. (The diameters of the circles indicate the estimated error.) Although the points are more scattered about this curve than the accuracy of the

Figs. 2 and 3.

the crystal found macroscopically is due to a gradual disintegration of the lattice as Roberts suggested.

Fig. 1 shows the Bragg angle as a function of the temperature in °C. The dashed curve measurement should permit, the quantitative agreement of the average $\alpha_\parallel = 16.1 \times 10^{-6}$

[3] R. C. Hergenrother, Thesis (1931). California Institute of Technology.

with Roberts' value (16.2×10^{-6}) is however surprisingly good.

The solid line indicates the best fitting curve drawn through the experimental points, showing that $\alpha_{\parallel}$ increases with temperature as far as the lattice expansion is concerned.

Special care was taken in the observations above 220°C where our measurements have shown a distinct deviation from Roberts' measurements, indicating that the macroscopic "decay" of the crystal is not caused by the lattice, since our $\alpha_{\parallel}$ continues even to increase beyond 230°.

The above relations are shown more clearly in Fig. 2 in which is plotted directly against the temperature. The dashed line is the curve given by Roberts which shows distinctly the decline of $\alpha_{\parallel}$ above 230°C. The solid line represents the values of $\alpha_{\parallel}$ obtained from the solid curve of Fig. 1, i.e., the best representation of our measurements in terms of $\alpha_{\parallel}$.

Since the specific heats of Bi between room-temperature and 700°C have been measured meanwhile by S. Umino[4] the validity of Grüneisen's postulate can be tested much more accurately than Roberts was able to do. Umino found a uniform increase in the true specific heats of Bi between 0° and melting point. Fig. 3 shows the curves obtained if the respective values of $\alpha_{\parallel}$ shown in Fig. 2 are divided by the corresponding values of c measured by Umino. The dashed curve represents the values of the macroscopic expansion, the solid line the lattice expansion. The fact that the latter does *not* show any temperature variation proves the validity of the postulate of Grüneisen and Goens for the lattice expansion parallel to the axis of Bi. The macroscopic expansion however is shown to deviate to a much larger degree from the relation than can possibly be explained by Roberts' experimental error.

Our observations together with those of Roberts seem to prove that there exists a distinct difference between the macroscopic and the lattice expansion. The spacing of the atoms in the lattice follows the $\alpha_{\parallel/c} = \text{const}$ relation up to the melting point, whereas the expansion of the crystal as a whole stays constant over a comparatively large region of temperature and begins to decline to nearly half its value during the last 30°–40° before the fusion.

Apparently we have the deal here with a phenomenon hithertofore unknown, which may be ascribed to the existence of a secondary structure in a macroscopic crystal, the thermal variation of which cannot be found by x-ray reflections due to its large parameter ($ca.\ 10^{-4}$ cm.)[5] A method however which integrates overall thermal variations in a large crystal, such as the usual measurement of thermal expansion, is bound to obtain different results, in case such a substructure exists as was already made highly probable in the case of Bi. With this assumption the "decay" of the macroscopic expansion had to be ascribed to a gradual disintegration of the secondary structure, which does not affect the crystal elements and therewith the x-ray reflections.

A detailed description of the methods and observations together with a more extended discussion of this effect will be published soon.

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[4] S. Umino, Sc. Rep. Tohoku Univ. **15**, 604 (1926).
[5] A. Goetz, Proc. Nat. Acad. **16**, 99 (1930).

A New Long Wave-Length Absorption Band of CS_2

In a recent paper C. R. Bailey and A. B. D. Cassie (Proc. Roy. Soc. **A132A**, 236 (1931)) have reported the result of an investigation of the infrared spectrum of CS_2 with a prism spectrometer. They observed four bands at 2330, 2179, 1523, and 878 cm^{-1} of which the band at 1523 was found to be much the most intense. All bands (except one which was not resolved) showed a simple doublet structure with a mean spacing of about 13 cm^{-1}. The Raman spectrum of CS_2 has also been measured (Krishnamurti, Ind. J. Phys. **5**, 109 (1930)) and consists of two lines at 655.5 and 795.0 cm^{-1} of which the first was found to be strong and the latter weak. These data may be examined in the light of the selection rules proposed by Dennison (Rev. Mod. Phys. **3**, 297 (1931)) with the view of determining the form of the molecule. While the number of bands so far observed is few, their positions distinctly favor the assumption that the molecule is both linear and symmetrical, since no