

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 α_{\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 α_{\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 α_{\parallel} above 230°C . The solid line represents the values of α_{\parallel} obtained from the solid curve of Fig. 1, i.e., the best representation of our measurements in terms of α_{\parallel} .

Since the specific heats of Bi between room-temperature and 700°C have been measured meanwhile by S. Umino⁴ 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 α_{\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.

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 meas-

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).

ured (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

band is observed whose frequency is equal to the sum or difference of any two observed bands. On the other hand differences between observed infrared bands do correspond exactly to the Raman frequencies.

Assuming that the molecule is linear and symmetrical we would conclude that the strong band at 1523 cm^{-1} is the active fundamental ν_3 (with the notation employed by Dennison, *l.c.* p. 292). Of the two Raman lines we would suppose that one should represent the inactive frequency ν_1 and that the other is twice the active fundamental ν_2 . From a paper by G. Placzek (*Zeits. f. Physik* **70**, 84 (1931)) on the intensity of Raman lines of molecules of this type it would appear very probable that the stronger line at 655.5 cm^{-1} is the inactive fundamental.

To test these ideas we have made a search for the active fundamental ν_2 in the region of 25μ . The spectrometer used employed a reflection grating of the echelette type. The thermopile window was of KBr. To prevent overlapping spectra a band of radiation from 21 to 34μ was obtained by reflection from a fluorite crystal. The observations were further freed from effects of short wave-length impurity by use of a fluorite plate as shutter. The absorption cell, which was 3 cm long and fitted with lacquer film windows, contained CS_2 vapor saturated at room temperature (26°C).

A very intense absorption band was found whose envelope structure could be obtained although the individual rotation lines were not resolved. The envelope possessed P , Q , and R branches lying at 389.4 , 396.8 , and 405.8 cm^{-1} respectively. Thus the existence and position of the band as well as its structure (existence of a Q branch) are completely in accord with our theory. The doublet separation, 16.4 cm^{-1} , leads to a moment of inertia $I = 172 \times 10^{-40}$ and a distance between S atoms of $2.54 \times 10^{-8}\text{ cm}$. These values are considerably lower than the figures obtained by Bailey and Cassie ($I = 264 \times 10^{-40}$ and $\text{S-S} = 3.20 \times 10^{-8}\text{ cm}$), but it appears possible that our results might be the more accurate by reason of the larger dispersion obtainable in this region.

A very important paper has appeared recently by E. Fermi (*Zeits. f. Physik* **71**, 250 (1931)) dealing with the Raman spectrum of symmetrical, linear tri-atomic molecules. Fermi has shown that for such molecules important modifications must be made in the

existing theory when one of the frequencies ν_1 is approximately equal to twice the frequency ν_2 . These modifications show on the one hand that the Raman spectrum should consist principally of two lines. On the other hand they show that the energy levels of the molecule may possess perturbation terms which are of first order in contradistinction to the usual theory in which the perturbations are always of second order. The first order perturbation whose existence Fermi has pointed out may be shown to go over into the usual second order perturbation expression when the difference between ν_1 and $2\nu_2$ is large compared with certain of the anharmonic constants. We have substituted the experimental values for the infrared and Raman frequencies of CS_2 into the theoretical formulae and find that for this case $\nu_1 - 2\nu_2$ is sufficiently large so that the energy levels may be described in the usual manner using second order terms. The molecule of CO_2 differs from CS_2 in that $\nu_1 - 2\nu_2$ is very nearly zero and thus the positions of the bands show certain anomalies which are however beautifully explained by the Fermi theory. It might be mentioned that the circumstance of $\nu_1 \cong 2\nu_2$ does not alter the validity of the selection rules.³

Our interpretation of the CS_2 spectrum is given in Table I and agrees completely with

TABLE I.

Identification	Frequency (obs.)	Frequency (calc.)
ν_2	396.8 cm	—
ν_1	655.5	—
$2\nu_2$	795.0	793.6
ν ν_1	878	867.5
ν^3	1523	—
$\nu_3 + \nu_1$	2179	2178.5
$\nu_3 + 2\nu_2$	2330	2318

the scheme proposed by Placzek. The exactness with which the combination relations are obeyed is a verification of our calculation which showed that the energy levels of CS_2 might be described with the aid of perturbations terms of second order only.

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