TABLE I. *Fundamental frequencies of the molecules of CH_4, CH_3D, CH_2D_2, CHD_3, CD_4.*

CH_4	(2914)	(1520)		3014			1304		
$(CH_3D)_+$	2944 $\parallel$	1460 $\perp$		2183 $\parallel$,		3013 $\perp$	1300 $\parallel$,		1151 $\perp$
$(CH_3D)_-$	2694 $\parallel$	1406 $\perp$		2993 $\parallel$,		2796 $\perp$	1036 $\parallel$,		1289 $\perp$
$(CH_2D_2)_+$	2141 M	(1317),	1424 M	2227 G,	2969 M,	3013 L	1228 G,	1019 M,	1082 L
$(CH_2D_2)_-$	2461 M	(1317),	1245 M	2768 G,	2771 M,	2536 L	989 G,	1089 M,	1285 L
$(CHD_3)_+$	2101 $\parallel$	1286 $\perp$		2992 $\parallel$,		2222 $\perp$	994 $\parallel$,		1020 $\perp$
$(CHD_3)_-$	2475 $\parallel$	1136 $\perp$		2166 $\parallel$,		2549 $\perp$	1163 $\parallel$,		1007 $\perp$
CD_4	(2061)	(1075)		2227			987		

with the four normal frequencies it is found that,

$$A=7.670\times10^5 \text{ dynes/cm} \qquad D=\pm1.278,$$
$$B=0.476 \qquad E=0.313.$$
$$C=0.341.$$

The fundamental frequencies of the molecules CH_3D, CH_2D_2, CHD_3 and CD_4 may now be calculated using the equations developed by Dr. Rosenthal.[5] There are two solutions corresponding to the positive and negative values for the constant D. Our results are collected in Table I. The inactive frequencies are enclosed in brackets. In the case of CH_2D_2 the letter following the frequency indicates whether the electric moment vibrates along the axis of least, middle or greatest moment of inertia.

Professor Barker and Mr. Ginsburg have continued their investigation of the absorption spectra of the heavy methanes and they have very kindly allowed us to state that their results appear to conform very satisfactorily with the bands predicted by the solution using $D=+1.278$. The band reported by them[6] at 1090 cm^{-1} is thus probably due to CH_2D_2. If this identification is correct, it would of course invalidate their estimate of the moment of inertia of methane.

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December 13, 1934.

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The Temperature Function of X-Ray Reflection in the Neighborhood of the Melting Point of a Crystal

In connection with some more extended work concerning the temperature variations of physical properties of metal crystals the following deviations from the Debye-Waller function concerning the temperature dependence of x-ray reflections have been observed in the neighborhood of the melting point of Bi crystals.

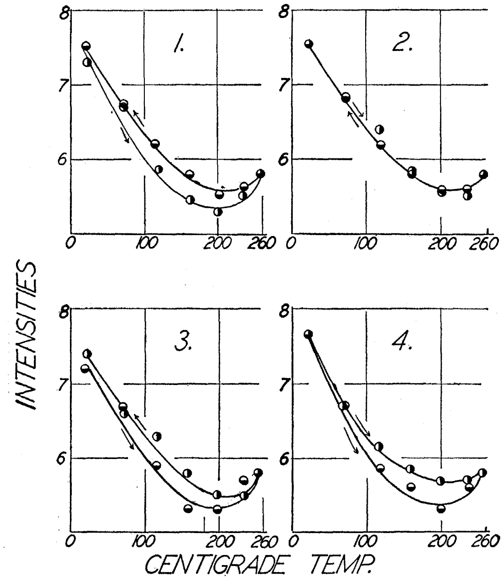
The apparatus used was the Bragg-spectrometer with stationary ionization chamber, described previously,[1] with added arrangements for heating the crystal in a neutral atmosphere under well controlled temperature conditions up to the melting point of Bi (272°C). The direction was along [111], the radiation used Mo $K\alpha$ in third order.

Whereas the Debye-Waller law requires a continuous decline with increasing temperature for the relative integrated intensity following:

$$I/I_0=e^{-kT\cdot\sin^2\theta}$$

it was found that at approximately 210°C I/I_0 passed through a minimum after which it *increased* with T to a value equivalent to $T\sim150°\text{C}$ for the highest observed temperature (265°C) (Fig. 2).

The reversibility of the $I/I_0(T)$ function proved to be largely depending upon the thermal history of the crystal although only crystals without any indication of crystallographic irregularities were used. Figs. 1 and 3 represent the $I/I_0(T)$ function of crystals having been raised to approximately 220°C and then quenched in liquid air



FIGS. 1–4. The ordinate represents the relative integrated intensity of third order Mo $K\alpha$ radiation reflected from Bi (111); the abscissae the temperature in C. In Figs. 1 and 3 the crystal was "quenched" before measurements with increasing temperatures were taken. In Fig. 2 the crystal was annealed before measurement. In Fig. 4 the crystal was heated after annealing (upper curve), then quenched and reheated (lower curve). The arrows indicate the temperature direction of the measurement.

previous to the heating necessary for the measurement. As is to be expected a certain "recrystallization" takes place inside the crystal indicated by a higher reflectivity for decreasing temperatures.

Fig. 2 shows the function of a crystal having been annealed at high temperature for a considerable time. Here the hysteresis is absent within the margin of experimental error.

The crystal in Fig. 4 is heated after annealing (upper curve) then immediately quenched and reheated. Here as in all other cases it will be noticed that a heated (and thus annealed) crystal being measured while cooling or a previously annealed crystal being heated shows a *higher* reflectivity, whereas the non-annealed crystal follows the power type of curve, i.e., is a less perfect reflector. It is interesting to note that this hysteresis is largest in the region of the anomaly $(d(I/I_0)/dT \sim 0)$.

A detailed account of the determination of the temperature function in a temperature range from the boiling point of hydrogen to the melting point of Bi will be published soon.

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December 5, 1934.

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