Proton Magnetic Resonance in Polyethylene

Roger Newman

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TABLE I. Compressibility of rocksalt at different temperatures in 10^{-13} cm²/dyne.

Temperature °K	Experimental k Adiabatic	Experimental k Isothermal	k calculated from curves
500	47.6	52 6	50
600	50 1	56	52
700	54.1	62	56
800	59.3	68	58
900	61.4	72	63
1000	65.7	85	73
1070	63.7	89	76

The method can be used at low temperatures where the bracket quantity is unimportant. The experimental values of C_v, E, and α can be used, so that the results become independent of any theory of crystal vibration. The values of p_1 can then be used in obtaining an accurate expression for the potential energy as a function of the volume. Such calculations are in progress.

I wish to thank Professor R. S. Krishnan for his interest in this investigation.

[1] Herzfeld and Mayer, Phys. Rev. 49, 995 (1935)
[2] Kane, J. Chem. Phys. 7, 603 (1939).
[3] Walther, Haschkowsky, and Stvelkow, Physik. Zeits. d. Sowjetunion 12, 35 (1937).
[4] Gruneisen, Handbuch der Physik, Vol. X.
[5] Hunter and Seigel, Phys Rev. 61, 84 (1942).
[6] Huggins and Mayer, J. Chem. Phys. 1, 643 (1933)

Ultrasonic Velocity of Sound at 12 Mc in Liquid Sulfur

O. J. KLEPPA
Institute for the Study of Metals, University of Chicago, Chicago, Illinois
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IN other communications[1,2] the author has reported the application of the pulse-circuit technique to measure the ultrasonic velocity of sound in liquid metals The present communication refers to the application of the same technique for the measurement of the velocity of sound in liquid sulfur. Over a period of about four days a total of 29 separate measurements at temperatures from 115° to 315°C was carried out on a sample of liquid sulfur prepared from "Sulfur Sublimed, U.S.P. XII" (Mallinckrodt). The results of these measurements are plotted in Fig. 1. The data recorded in Table I were obtained from the smooth curve drawn through the experimental points.

It will be seen that there is no simple linear relationship between sound velocity and temperature. In fact, it appears that the curve in Fig. 1 has an inflection point in the transition region 160°–220°C, where the maximum viscosity is found. It should be pointed out that it was never possible to detect any hysteresis in the measured values for sound velocity during heating or cooling through this region.
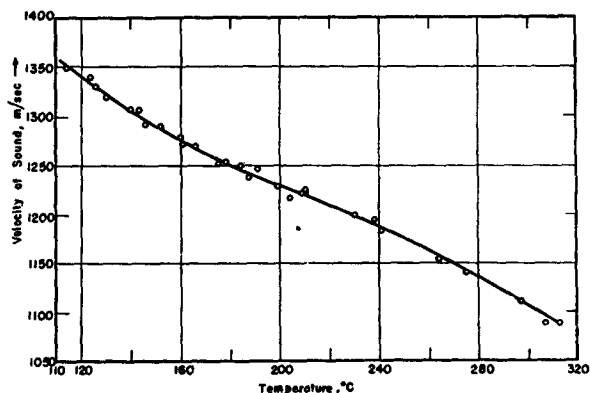

FIG. 1. Sound velocity as function of temperature.

TABLE I. Velocities of sound in liquid sulfur

Temperature, °C	Sound velocity (m/sec.)
115	135_0
150	129_0
200	123_0
250	117_5
300	110_5

Adiabatic and isothermal compressibility of liquid sulfur:—International Critical Tables' report for the density of liquid sulfur at 115°C, $\rho = 1.808$ g cm^{-3}, for the specific heat, $C_P = 7.27$ cal deg.$^{-1}$ and for the coefficient of thermal expansion, $\alpha = 4.3 \times 10^{-4}$ deg.$^{-1}$. Making use of these data we compute for liquid sulfur at 115°C:

Adiabatic compressibility, $K_S = 30.4 \times 10^{-6}$ bar^{-1}
Isothermal compressibility, $K_T = 34.6 \times 10^{-6}$ bar^{-1}.

Thus, $C_P/C_V = 1.14$ and specific heat, $C_V = 6.3_8$ cal. deg.$^{-1}$. The compressibility data may be compared with the isothermal compressibility of orthorhombic sulfur at 20°, which by I.C.T. is reported to be 13.1×10^{-6} bar^{-1}. The data thus indicate a very large increase in compressibility on fusion compared to what is found in the case of metals. These, in general, show an increase on fusion of about 15 percent only, while the same figure for sulfur appears to be of the order of 100 percent or more.

[1] O J Kleppa, J. Chem. Phys. 17, 668 (1949).
[2] O J. Kleppa, J. Chem Phys. (to be published).

Proton Magnetic Resonance in Polyethylene

ROGER NEWMAN*
Lyman Laboratories, Harvard University, Cambridge, Massachusetts
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IN the course of some studies of the proton magnetic resonance in high polymers, a line-width transition was observed in polyethylene. Figure 1 summarizes the results. Figure 1a shows the line shape of the resonance at −186° and 25°C. Figure 1b shows the line width[1] as a function of temperature. As can be seen from the figure the midpoint of the line-width transition lies at about −38°C.
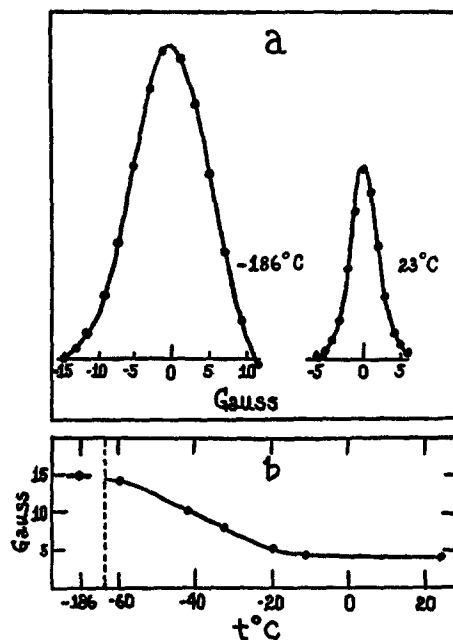

FIG. 1. Line shape data for polyethylene

It will be recalled that a transition, as shown by a change in the coefficient of expansion, has been reported at $-40°C$ for this polymer.[2] The line-width transition reported here occurs at very closely the same temperature. However, the coincidence of the two effects may be accidental. Hunter and Oakes have described their effect as being due to a "freezing in" of the motion of the polymer segments. That is, at temperatures below the transition point, the mean thermal energy is presumably insufficient to allow passage of the chain segments with sufficient frequency over whatever potential barriers separate their equilibrium positions. Such a description would of course account for the line-width transition as observed here.[3]

Using a procedure described elsewhere,[3] a rough estimate of the height of the aforementioned potential barriers can be made It should of course be appreciated that for something whose motions are as complicated as those of a polymer a measured "barrier height" must be a rather loosely defined term. Any number, such as that obtained here, probably represents no more than some sort of suitably weighted average. With this reservation in mind, the present data suggest a barrier height of about 7 kcal./mole. A more accurate value probably could have been obtained from a nuclear relaxation time study, but the latter was precluded by instrumental difficulties. It is of some interest to note that in polyethylene sebacate, the dielectric dispersion data indicated a barrier height of 12 kcal./mole.[4] In the sebacate it might be expected that the interactions of the strong polar groups would tend to raise the existing potential barriers over what they would be for polyethylene, which is perhaps borne out by the data.

The resonance line shows no suggestion of structural features down to liquid nitrogen temperatures. This is in agreement with the results of Andrew, who studied several long chain paraffins.[5] Polyethylene is, of course, simply a paraffin molecule of tremendous length.

The second moment of the polyethylene resonance at $-186°C$ is 28 ± 2 gauss[2]. On the basis of a zig-zag chain structure the intermolecular contribution to the second moment would be about 19 gauss[2]. A reasonable maximum value for the contribution due to intramolecular or folded chain interactions would be about 8 gauss[2].[5] The maximum total second moment would then be about 27 gauss[2], which is of the same order as the observed moment A closer comparison of the two values does not seem justified.

I should like to thank Drs. Buchdahl and Nielson of Monsanto for a helpful discussion of this work.

* Du Pont Postdoctoral Fellow in Chemistry (1949–50).
[1] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. 16, 1164 (1948)
[2] E. Hunter and W. Oakes, Trans. Faraday Soc. 41, 49 (1945).
[3] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. 18, 162 (1950).
[4] W. A. Yager and W. O. Baker, J. Am. Chem. Soc. 64, 2164 (1942)
[5] E R. Andrew, J. Chem Phys. 18, 607 (1950).

The Development and the Surface Energy of the Planes of the Primary Rhombohedron in α-Quartz

B. D. Saksena and L. M. Pant
Department of Physics, University of Allahabad, India
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QUARTZ shows a large development of form. The three principal development forms are the faces of the primary and inverse rhombohedra and the hexagonal prism faces which are found in most crystals. Of these, the faces of the primary rhombohedron are found highly developed even in small specimens. To explain this, Beckenkamp[1] located the Si—O bonds along the edges joining the faces of the primary and inverse rhombohedra, but this prediction is not verified by x-ray data. By projecting the unit cell of α-quartz on a rhombohedral pattern, we have been able to show that the silicon-oxygen bonds in quartz lie very close

to the planes of the primary rhombohedron, and it appears likely that this is the cause of the large development of these planes.

The coordinates of the atoms in the unit cell of left quartz with respect to the hexagonal axes (a, a, and c) are (Wyckoff)[2]:

Silicons (1, 2, 3, 4, 5, 6)—$(u, 0, 0)$, $(1-u, 1-u, \frac{1}{3})$, $(0, u, -\frac{1}{3})$, $(\overline{1-u}, 0, 0)$, $(\bar{u}, \bar{u}, \frac{1}{3})$, $(0, \overline{1-u}, -\frac{1}{3})$

Oxygens (7, 8, 9, 10, 11, 12)—(x, y, z), $(y, x, \bar{z}+\frac{2}{3})$, $(\bar{y}, x-y, z-\frac{1}{3})$, $(\bar{x}, y-x, \bar{z}+\frac{1}{3})$, $(y-x, \bar{x}, z-\frac{2}{3})$, $(x-y, \bar{y}, \bar{z})$.

To represent the atoms on a rhombohedral pattern we take three equal axes inclined at angles of $93°57'$ to one another, and then find the corresponding hexagonal axes. These are seen from Fig 1 to be OF, OB, OD, and OO' where OF=OB=OD=a and
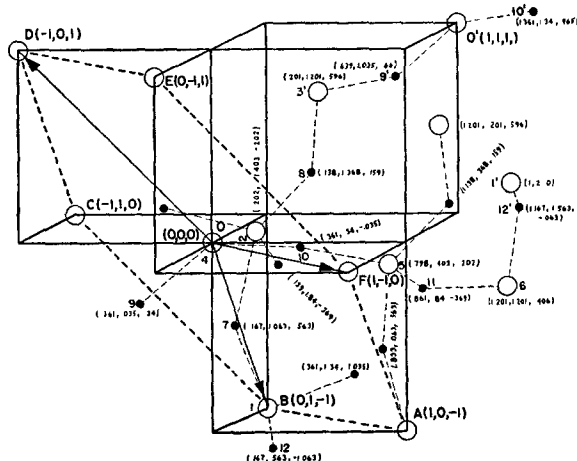

FIG 1. Positions of the atoms in left quartz.

OO'=c, the ratio c/a being equal to 1.1. The silicon atoms situated at the center and the corners of the hexagon ABCDEF and at the point O' are equivalent atoms. By joining the point O' to the corners of the hexagon, we get the hexagonal pyramid of quartz whose alternate planes O'AF, O'BC, O'DE are the rhombohedral planes (1, 0, 0) (0, 1, 0), and (0, 0, 1). It is easy to see that if the hexagonal axes are taken in the order OF, OB, and OD (OF facing the observer), the above planes are also the planes of the primary rhombohedron for left quartz. Since we may locate the origin of the coordinates in the unit cell on either OF, OB, or OD, we suppose it to lie between the points O and B at a distance "u" from B. The hexagonal coordinates (e, f, g), referred to the axes parallel to OB, OD, and OO' through this origin, may now be converted into rhombohedral coordinates (p, q, r), having their origin at the point (0, 0, 0), by the relations given below

$$p = -f + g, \quad q = (1-u) + e + g, \quad r = f + g - e - (1-u)$$

The rhombohedral coordinates of the atoms in the unit cell, using the x-ray data of Wei,[3] $u=0.465a$, $x=0.417a$, $y=0.278a$, $z=0$ $111c$, are shown in Fig. 1. It is seen that two of the Si—O bonds at each silicon atom lie very close to the planes of the primary rhombohedron. If we slightly alter the coordinates to $u=0.47a$, $x=0.42a$, $y=0.31a$, and $z=0.11c$, the bonds are found to lie exactly in these planes. Thus the two Si—O bonds joining the silicon O' to the oxygen atoms 9' and 10' now have the direction-ratios (1, 0, 1) and (1, 1, 0) respectively, and therefore lie in the planes (0, 1, 0) and (0, 0, 1) of the primary rhombohedron for left quartz, along the lines joining the point O' to the middle points of the lines CB and DE. On changing the sign of the z coordinate, i.e , considering the case of right quartz, we obtain the same result. It is noticed that the same bonds now lie in the planes of the inverse rhombohedron for left quartz and, therefore, in the planes of the primary rhombohedron for right quartz.