

Elastic Wave Velocity Effect on Temperature Diffuse Scattering in Cubic Powders

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A simplifying assumption made in previous calculations of temperature diffuse scattering (TDS) for cubic powders is that all elastic waves have the same average velocity. In practice, the longitudinal velocity is found to be about twice the magnitude of the transverse velocity. The effect of such velocity differences is considered for the one- and two-phonon contribution to TDS. It is found that the major effect in both the one- and two-phonon contribution is to sharpen the peaking of TDS in the vicinity of the Bragg peaks. For the most part, there is a decrease of the magnitude of TDS in the valleys between Bragg peaks and an increase in the magnitude of TDS at the Bragg peaks over the results of the previous calculations. Thus, the observed magnitude of TDS between Bragg peaks is decreased, in accord with comparisons of earlier theory with experiment. The contribution of TDS to the apparent measured integrated intensity is found to be larger than earlier estimates and thus increases the importance of correcting for the TDS contribution to measured Bragg intensities.

Introduction

Warren (1953) and the author (1958) have developed expressions for the temperature diffuse scattering (TDS) in cubic powders. A simplifying assumption made in these calculations is that all the elastic waves have the same average velocity. In practice, the longitudinal velocity is found to be about twice the magnitude of the transverse velocity. We here extend the previous TDS calculations for cubic powders (Warren, 1953; Paskin, 1958; Chipman & Paskin, 1959) so as to include the explicit longitudinal and transverse velocity dependence. Theoretical relationships are derived for the intensity of TDS as a function of the wave velocities and parameters that depend on the position in reciprocal space. Calculations have been made for both the one- and two-phonon contributions (Paskin, 1958; Chipman & Paskin) and have been numerically evaluated for a wide region of reciprocal space. The one-phonon calculation is an extension of the previous work of the author (1958) and the two-phonon calculation combines in approximate manner the author's previous two-phonon calculation (1958) with some related work by Walker (1956).

One-phonon TDS calculation (theory)

From previous work (Paskin, 1958; Chipman & Paskin) it can be shown I_{TDS} , the intensity of the one-phonon contribution to TDS, may be written as

$$I_{\text{TDS}} = (\mathcal{S} g_{\text{max}}^2 \langle V^2 \rangle g^{-2} / 3) \sum_{\varphi j} V_{\varphi j}^{-2} \cos^2 \alpha_{\varphi j}, \quad (1)$$

where \mathcal{S} is a parameter (subsequently defined in detail) which depends on the Debye-Waller factor and the atomic scattering factor,

$$\langle V^2 \rangle = 3[(V_l^{-2} + 2V_t^{-2})_{\text{average}}]^{-1}$$

is a Debye-like average velocity in terms of V_l , the longitudinal velocity and V_t , the transverse velocity, g_{max} is the radius of a sphere equal to each Brillouin zone, g is the magnitude of the reciprocal wavelength of the elastic wave, $V_{\varphi j}$ is the velocity of the elastic wave φj and $\alpha_{\varphi j}$ is the angle between the X-ray diffraction vector and the vibration direction of the wave.

In the previous and present calculations, it is assumed that the crystal is elastically isotropic. Consequently, the waves of a given wave vector can be resolved into a longitudinal and two transverse components (with equal wave velocities). In previous work (Warren, 1953; Paskin, 1958) it was further assumed that the longitudinal velocity V_l is equal to the transverse velocity V_t and thus

$$\langle V^2 \rangle \sum_{\varphi j} V_{\varphi j}^{-2} \cos^2 \alpha_{\varphi j} = \langle V^2 \rangle V_t^{-2} \sum_{\varphi j} \cos^2 \alpha_{\varphi j} = 1. \quad (2)$$

In actuality, for common materials $V_l \cong 2V_t$ and thus (2) is not valid. It is not immediately apparent whether the approximation in (2) under- or over-estimates the term. Subsequently, we find that the term when appropriately averaged can be both greater or less than unity depending on both the distance from a Bragg peak and the relative separation of the Bragg peaks in the vicinity. This is readily seen in the detailed results of retaining the V_l and V_t terms in the equation for the intensity. The contribution to the powder pattern intensity arising from all the contributing Brillouin zones from a given (hkl) peak at a fixed position in reciprocal space is

$$\langle I_{\text{TDS}}(V_l, V_t, X) \rangle_{hkl} = \int_{X_{\text{min}}}^{X_{\text{max}}} [I_{\text{TDS}} / (2X X_{hkl})] \mathcal{G} d\mathcal{G}, \quad (3)$$

where a = edge of a cubic cell, λ = wave length of X-rays, $X = 2a \sin \theta / \lambda$, $X_{hkl} = 2a \sin \theta_{hkl} / \lambda =$

$(h^2+k^2+l^2)^{1/2}$, $\mathcal{G} = ag$, $X_{\min.} = ag_{\min.} = |X - X_{hkl}|$ and $X_m = ag_{\max.}$. Multiplying by the appropriate multiplicity factor and adding values from all peaks that can contribute at fixed value of X , the total TDS powder intensity, $\langle I_{\text{TDI}}(V_l, V_t, X) \rangle$ is

$$\langle I_{\text{TDI}}(V_l, V_t, X) \rangle = \sum_{hkl} [j_{hkl}/(2X X_{hkl})] \int_{X_{\min.}}^{X_m} I_{\text{TDI}} \mathcal{G} d\mathcal{G}. \quad (4)$$

In order to perform the integration in (4), we first put the direction cosine terms of I_{TDI} in terms of X , X_{hkl} and \mathcal{G} . Thus, the longitudinal term is written as

$$\left\langle \frac{\cos^2 \alpha_l}{V_l^2} \right\rangle = \frac{\cos^2 \alpha}{V_l^2} = \left(\frac{X_{hkl}^2 - X^2 - \mathcal{G}^2}{2X\mathcal{G}} \right)^2 \frac{1}{V_l^2}, \quad (5)$$

where α (shown graphically in Fig. 1) is the angle (in the $X-X_{hkl}$ plane) between \mathcal{G} and X . The two

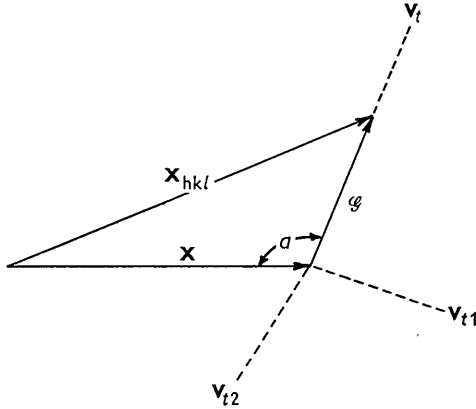


Fig. 1. Vector diagram of the relationship between the X-ray photon wave-vector X , the elastic wave phonon wave-vector \mathcal{G} , and X_{hkl} , the vector to the (hkl) reciprocal lattice point. V_l , V_{t1} and V_{t2} indicate the orientations of the longitudinal and two possible transverse waves for the given phonon wave-vector \mathcal{G} .

transverse terms have equal velocities and are at right angles to each other as shown in Fig. 1. In replacing the direction cosine terms by functions of X , X_{hkl} and \mathcal{G} we make use of the fact that the desired factor is the spacial average of these terms. In the case of the longitudinal term, (5) is directly the spacial average. In the case of the transverse term, the appropriate spacial average results in the following

$$\left\langle \frac{\cos^2 \alpha_{t1}}{V_t^2} + \frac{\cos^2 \alpha_{t2}}{V_t^2} \right\rangle = \frac{\sin^2 \alpha}{V_t^2} = \left[1 - \left(\frac{X_{hkl}^2 - X^2 - \mathcal{G}^2}{2X\mathcal{G}} \right)^2 \right] \frac{1}{V_t^2}. \quad (6)$$

Making use of (1), (4), (5) and (6) we arrive at the following expression:

$$\langle I_{\text{TDI}}(V_l, V_t, X) \rangle = \mathcal{F}(C_1 + \delta C'_1), \quad (7)$$

where

$$C_1 = \frac{X_m^2}{12X} \sum_{hkl} \frac{j_{hkl}}{X_{hkl}} \ln \left[\frac{X_m^2}{(X - X_{hkl})^2} \right], \quad (8)$$

$$\delta = \langle V^2 \rangle (V_t^{-2} - V_l^{-2}) > 0, \quad (9)$$

$$C'_1 = \frac{X_m^2}{12X} \sum_{hkl} \frac{j_{hkl}}{X_{hkl}} \left\{ \left[\left(\frac{X^2 + X_{hkl}^2}{2X^2} \right) - \frac{2}{3} \right] \times \ln \left[\frac{X_m^2}{(X - X_{hkl})^2} \right] - \frac{X_{hkl}}{X} + \frac{(X^2 - X_{hkl}^2)^2}{4X_m^2 X^2} - \frac{X_m^2}{4X^2} \right\}, \quad (10)$$

and

$$\mathcal{F} = Nf^2(2M_D) \exp(-2M). \quad (11)$$

Here N = the number of atoms, f = the atomic scattering factor, $2M$ = the Debye-Waller factor and $2M_D$ the TDS modified Debye-Waller (Paskin, 1958). Although a detailed discussion of $2M_D$ is beyond the scope of this paper (see Chipman & Paskin for details), for most materials it would be expected that $2M_D$ is approximately equal to $2M$. The form of (7) was chosen so as to consist of two terms: a term proportional to C_1 which in turn is identically the factor obtained in earlier calculations with $V_l = V_t$ and an additional or corrective term proportional to $\delta C'_1$. The explicit velocity dependence of the corrective term is contained in δ , and the reciprocal space dependence of the corrective factor is contained in C'_1 . δ , of course, reduces to zero when $V_l = V_t$ but in addition it has the convenient property of being unity when $V_l = 2V_t$, a good approximation for common materials. Therefore, C'_1 is to good approximation directly the corrective factor.

One-phonon TDS calculation (discussion)

In Fig. 2, the corrective term C'_1 is given as a function of X . The important points to note are: the velocity corrective term is generally negative in the region between Bragg peaks and positive in the immediate vicinity of a Bragg peak. In order to obtain a quantitative comparison of the additional velocity corrective term with the previous results, in Fig. 3 we have plotted C'_1/C_1 , the ratio of the velocity corrective term ($V_l = 2V_t$) to the previous results ($V_l = V_t$). It can be seen that the observable portion of TDS (i.e. the region between Bragg peaks) has been lowered by the velocity corrective term over that of previous calculations. This is qualitatively in agreement with the experimental observations of Chipman & Paskin. In order to obtain agreement with previous theory and experiment they found that they must use a value of $2M_D$ that is lower than $2M$ to match TDS in the region between Bragg peaks. This follows because the explicit inclusion of the velocity terms in the parameter multiplying \mathcal{F} lowers its value over that previously calculated. Thus, a good fit between previous theory and experiment could only be obtained by using a low value of $2M_D$ to compensate for the previous over-estimation of the parameter

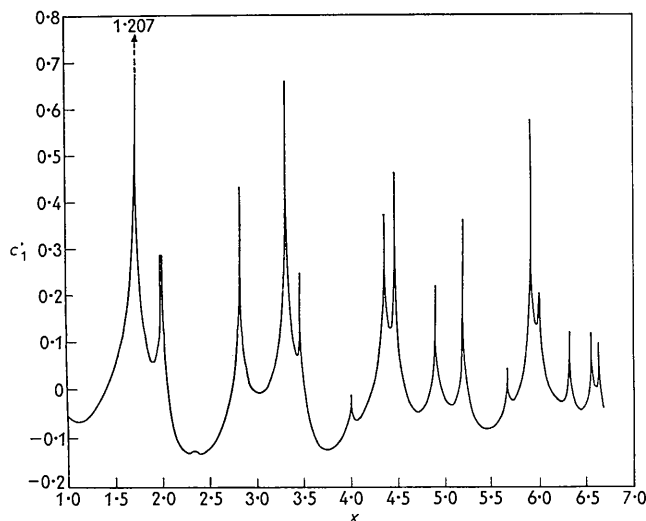


Fig. 2. C'_1 , the one-phonon velocity corrective term for the face-centered-cubic structure, as a function of X .

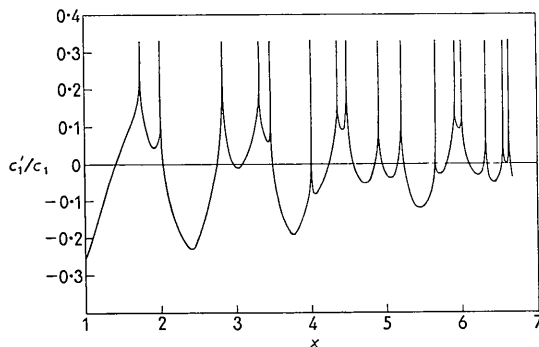


Fig. 3. The ratio of the one-phonon velocity corrective term ($V_l = 2V_t$) to the previous one-phonon results ($V_l = V_t$), for the face-centered-cubic structure, as a function of X .

multiplying \mathcal{S} . It is also noteworthy that the additional velocity dependent correction seems to be decreasingly important as one passes into the region of $X \gg 1$. This seems to follow from the fact that the velocity corrective term does not get the opportunity to get very negative when the peaks are closely spaced. In the region $X \gg 1$, the latter condition obtains and the velocity corrective term seems to hover about zero. The observation of the dependence of the velocity corrective term on the closeness of adjoining Bragg peaks, leads one to note that in the case of the close pairs of peaks or doublets, the corrective term remains positive between doublet peaks. Thus, the effect of the velocity corrective term is to increase TDS between Bragg doublets so that the TDS background in the region between peaks is actually much higher than the average TDS background in the exterior region. This is an important fact in trying to correct for the peaking up of TDS under the Bragg peak. It might be recalled that in practice TDS is important because it peaks

at the same point in reciprocal space as Bragg peaks occur. Thus, in measuring integrated intensities above a straight-line connecting points of the background, TDS is erroneously included in the integrated Bragg intensities. A complete discussion of this is given by Chipman & Paskin and one need here only note the additional contribution caused by the velocity corrective terms. Examining Fig. 3 it is apparent that the major effect of the velocity corrective terms is to cause sharper peaking of TDS and hence a greater contribution of TDS to the apparent measured integrated intensities. It is difficult to make a general quantitative estimate about the increased contribution of TDS to the measured integrated intensities over that previously calculated. The increase depends on the particular peak as well as the separation between peaks. We have however found the increase to range between about 10–30% for average peaks over that of previous estimates. This can be seen from Fig. 3 if one thinks of the valleys between peaks as making up the base lines and looks at the additional TDS contribution to the Bragg peak as the additional velocity dependent TDS contribution lying above this base line.

Chipman & Paskin have also noticed that there is an anomalous diffuse scattering in powders in the region $X \sim 1$ (below the (111) peak). The additional velocity corrective term seems to decrease the TDS in this region and thus to increase the magnitude of the anomalous extra scattering.

Two-phonon calculation (theory)

The previous two-phonon TDS calculation for powders was made with $V_l = V_t$ and assumed no dispersion. A simplifying assumption was made in the intermediate stage of calculation to obtain a simple closed form for I_{TD2} and in turn led to a closed form for the appropriate powder average of the intensity I_{TD2} . Walker (1956) in his calculation of I_{TD2} (directed toward single-crystal work) did not restrict himself to the case $V_l = V_t$ and in addition assumed a dispersion form appropriate to a one-dimensional linear chain. Fortunately, it was found that the author's work and Walker's formula (with V_l set equal to V_t) closely approximate one-another. Thus, although it was impractical to extend the author's previous calculation (1958) to the case $V_l \neq V_t$, an approximate closed-form solution to $I_{\text{TD2}}(V_l \neq V_t)$ could be obtained by combining the author's previous results with those of Walker (1956). As the effect of taking the powder average for the one- and two-phonon processes minimizes the importance of the contributions from the edges of the Brillouin zones, we have where ever possible chosen cruder approximations than would be possible in single-crystal work for the sake of a closed-form solution. Thus, the combination-closed-form chosen for I_{TD2} is only approximate as $V_l \gg V_t$ but does have the property of yielding the previous solution of the author (1958) as $V_l \rightarrow V_t$ and does contain

the essential behavior of I_{TD2} as a function of V_l and V_t . With this qualification, the equation chosen for I_{TD2} was

$$I_{\text{TD2}} = \frac{\mathcal{F} M_D X_m^4 k^2}{9\mathcal{G}(1+2k/3)^2} (A + B \sin^2 \alpha + C \sin^4 \alpha), \quad (12)$$

where

$$\begin{aligned} A &= k^{-2} + k^{-1} + 0.25, \\ B &= (k^{-1} + 0.5)/2, \\ C &= 3/32, \end{aligned}$$

and

$$1+k = V_l^2/V_t^2.$$

In going from Walker's equation for I_{TD2} to (12), we have made use of the following simplifying approximations: $\gamma_1 + \gamma_2 = 1$, $2\gamma_2 - 2\gamma_4 - \gamma_3 = 0$, $\gamma_4 = 0.25$ and $\pi^2 E_0/4 = X_m/\mathcal{G}$ (see Walker (1956) for the definitions of the above terms). Taking the appropriate powder average as given by (3), we arrive at the following equation for $\langle I_{\text{TD2}} \rangle$

$$\langle I_{\text{TD2}} \rangle = \mathcal{F} M_D \left\{ \left[\frac{k^2}{(1+2k/3)^2} \right] (A \varrho_A + B \varrho_B + C \varrho_C) \right\}, \quad (13)$$

where

$$\varrho_A = (\pi^3 X_m^4 X^{-1}/18) \sum_{hkl} X_{hkl}^{-1} j_{hkl} [X_m - |X - X_{hkl}|],$$

$$\begin{aligned} \varrho_B &= \frac{\pi^3 X_m^4}{54 X^3} \sum_{hkl} \frac{j_{hkl}}{X_{hkl}} \left\{ [3(X^2 + X_{hkl}^2) - X_m^2] X_m \right. \\ &\quad \left. - [3(X^2 + X_{hkl}^2) - (X - X_{hkl})^2] |X - X_{hkl}| \right\} \\ &\quad - \frac{\pi^3 X_m^3}{18 X} \sum_{hkl} j_{hkl} X_{hkl} \left[1 - \left(\frac{X_{hkl}^2 + X^2 - X_m^2}{2X X_{hkl}} \right)^2 \right], \end{aligned}$$

and

$$\begin{aligned} \varrho_C &= -\frac{\pi^3 X_m}{54 X} \sum_{hkl} j_{hkl} X_{hkl}^3 \left[1 - \left(\frac{X_{hkl}^2 + X^2 - X_m^2}{2X X_{hkl}} \right)^2 \right]^2 \\ &\quad - \frac{2\pi^3 X_m^4}{27 X^3} \sum_{hkl} j_{hkl} X_{hkl} (X_m - |X - X_{hkl}|) \\ &\quad - \frac{2\pi^3 X_m^3}{27 X^2} \sum_{hkl} j_{hkl} X_{hkl}^2 \left[\left(\frac{X_{hkl}^2 + X^2 - X_m^2}{2X X_{hkl}} \right)^3 \right. \\ &\quad \left. - \left(\frac{X_{hkl}^2 + X^2 - X_m^2}{2X X_{hkl}} \right) \right] \\ &\quad + \frac{\pi^3 X_m^5}{270 X^5} \sum_{hkl} \frac{j_{hkl}}{X_{hkl}} [8(X^2 + X_{hkl}^2)^2 + 4(X^2 + X_{hkl}^2) \\ &\quad \times (X_{hkl}^2 + X^2 - X_m^2) + 3(X_{hkl}^2 + X^2 - X_m^2)^2] \\ &\quad - \frac{\pi^3 X_m^4}{270 X^5} \sum_{hkl} \frac{j_{hkl} |X - X_{hkl}|}{X_{hkl}} [8(X^2 + X_{hkl}^2)^2 \\ &\quad + 8X X_{hkl} (X^2 + X_{hkl}^2) + 12X^2 X_{hkl}^2]. \end{aligned}$$

In Fig. 4, ϱ_A , ϱ_B and ϱ_C of (13) are plotted as a function of X . Unfortunately, there is no simple way of representing the general two-phonon results in such a way as to contain the $V_l = V_t$ result plus a corrective term—as was the case in the general one-phonon case. This is a consequence of the general two-phonon

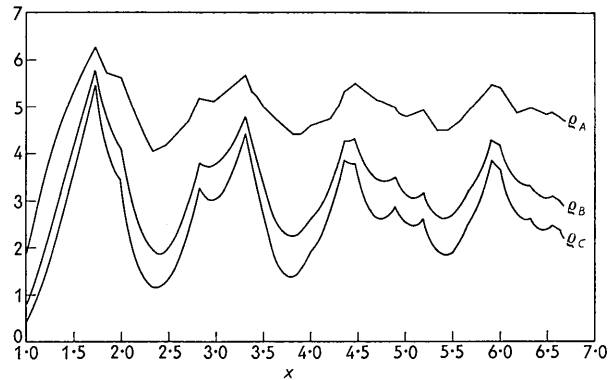


Fig. 4. ϱ_A , ϱ_B and ϱ_C , the two-phonon contributions, for the face-centered-cubic structure, as a function of X .

formulation having a velocity dependent factor multiplying each reciprocal space-dependent parameter, and these velocity dependent parameters do not happen to be simply related to the $V_l = V_t$ parameter. We therefore have resorted to calculating the two-phonon TDS for the $V_l = V_t$ case and the $V_l = 2V_t$ and directly comparing the ratios. For $V_l = V_t$, $k = 0$, and the braced term becomes ϱ_A which of course is identical to the previous result (Paskin, 1958) and in terms of the previous notation we denote this parameter as C_2 . For $V_l = 2V_t$, $k = 3$, and we denote the braced term as C'_2 . C'_2/C_2 is given in Fig. 5. This ratio

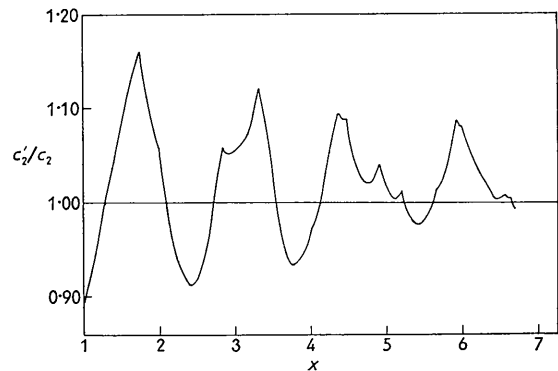


Fig. 5. The ratio of the two-phonon contributions for $V_l = 2V_t$ to that for $V_l = V_t$, for the face-centered-cubic structure, as a function of X .

is the ratio of the two-phonon TDS with $V_l = 2V_t$ to that with $V_l = V_t$ and thus enables a semi-quantitative examination of the velocity effects on the previous two-phonon TDS calculation (Paskin, 1958).

Two-phonon TDS calculation (discussion)

The important results of the present two-phonon calculation can be seen from Fig. 5 to be quite analogous to those of the one-phonon calculation: There is more pronounced peaking in the vicinity of the Bragg peaks and a general lowering of the TDS back-

ground in the region between Bragg peaks. Again the region between doublets is also higher than the general background. As in the case of the one-phonon calculation, the major effect relative to correcting for the TDS contribution to measured integrated intensities, is to increase the contribution. In the previous work of Chipman & Paskin, the two-phonon contribution to the apparent integrated intensity was neglected in arriving at a TDS correction in analytic form. It is apparent that in fact there is likely some contribution from the two-phonon TDS as well as the one-phonon. To the degree that the peaking of the two-phonon contribution becomes important, the approximate analytic expression given by Chipman & Paskin becomes in error and their graphical method must be utilized with the velocity term corrections as given

by this paper. However, in general for materials such as copper with usual Debye characteristic temperatures, the analytic formula will prove sufficient over the usual region of reciprocal space.

I am pleased to acknowledge many valuable discussions with Dr D. R. Chipman pertaining to the problem of TDS in cubic powders.

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The Crystal Structure of Orthorhombic Hexatriacontane $C_{36}H_{74}$

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Single crystals of the orthorhombic form of hexatriacontane $C_{36}H_{74}$ have been shown to have space group $Pca2_1$ with unit-cell dimensions $a = 7.42$, $b = 4.96$, $c = 95.14$ Å. The crystal structure has been determined from Fourier syntheses of the electron density projected down the three principal crystallographic axes and from observations of the agreement between observed and calculated structure factors. The molecular chains are regular and periodic within experimental error, with a C-C bond length of 1.533 Å and a zigzag bond angle of 112°. The side-by-side packing of chains is identical with that found in the monoclinic form and in polythene. Intermolecular distances are given and discussed briefly in relation to the polymorphism, the stability and the anisotropic thermal vibrations and expansion coefficients of long chain hydrocarbons.

Introduction

The structure of the monoclinic form of hexatriacontane has recently been described by Shearer & Vand (1956). The investigation described here was in progress at the same time as the work of these authors, and the results are now presented as a contribution to the study of long-chain hydrocarbons and their polymorphism. The crystals examined in this investigation were part of the original batch of material used by Vand (1953) and Shearer & Vand (1956), and were originally prepared by Dr McGowan of I.C.I. (Alkali) Ltd., by a Wurtz synthesis from octa-decyl iodide $C_{18}H_{37}I$. When the original material was recrystallized from high-boiling petroleum only small, poor-quality crystals were obtained. Crystals satisfactory for X-ray intensity measurements were

finally grown by dissolving the recrystallized material in hot petroleum ether and cooling slowly over a period of a few days in a large water-filled Dewar vessel. Orthorhombic plate-like crystals were obtained with inter-edge angles of 67° 30'. The large plane surfaces are (001) faces and the edge surfaces are (110) and ($\bar{1}\bar{1}0$) faces. In subsequent experiments it was found that monoclinic crystals were obtained by crystallization from benzene and that the orthorhombic form was usually obtained from petroleum ether. These observations will be discussed later in the light of Smith's (1953) and Vand & Shearer's work, but at the time we chose to examine the crystal structure of the orthorhombic form because of its closer analogy to the crystal structure of polythene described by Bunn (1939). The crystallographic data for this form has already been used in the derivation of bond polarizabilities (Bunn & Daubeny, 1954).

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