core); this, however, can easily be enlarged. By means of a subroutine, indexes and moduli are computed and stored in the core for all reciprocal- and direct-lattice vectors which are contained within the spheres of radii h_0 and l_0, respectively, and are not related by a centre of symmetry. Ewald series (3) is calculated by another subroutine for all interatomic vectors $\mathbf{x}_{ij}$ which are not symmetry-related, using the relation $|\mathbf{x} \pm \mathbf{l}| = x^2 + l^2 \pm \sum_{1}^{3}{}_p\, l_p \left(\sum_{1}^{3}{}_q\, G_{pq} x_q\right)$, where the G_{pq}'s are metric tensor elements. The output of the program shows: the total electrostatic lattice energy of a mole, E, and its two components E_1 and E_2, the coefficients (9) and (10) and the coefficients referring to the independent ionic species. As an example, running the program on K_2SO_4 in the optimal convergence conditions required 5·5 s of execution time on an IBM 370/158 computer.

APPENDIX II

The triple integral in (12) was calculated in spherical coordinates assuming $\theta = 0$ for the direction of vector $\mathbf{x}$. In the first step, the substitution $t = A\sqrt{(l^2 + 2xl\cos\theta + x^2)}$ was used:

$$\int_0^{\pi} \frac{\operatorname{erfc}[A\sqrt{(l^2 + 2xl\cos\theta + x^2)}]}{\sqrt{(l^2 + 2xl\cos\theta + x^2)}} \sin\theta \, \mathrm{d}\theta$$

$$= \frac{(l+x)\operatorname{erfc}[A(l+x)] - (l-x)\operatorname{erfc}[A(l-x)]}{xl}$$

$$- \frac{\exp[-A^2(l+x)^2] - \exp[-A^2(l-x)^2]}{\sqrt{(\pi)}Axl};$$

multiplying this function by $l^2 \mathrm{d}l$ and integrating by parts repeatedly between the limits l_0 and $+\infty$ gave the result of (12).

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Comparisons of Atomic Thermal Motions for Graphite at 300 K Based on X-ray, Neutron, and Phonon-Spectrum Data

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The mean-square amplitudes of vibration in graphite based on an X-ray charge-density analysis are 0·0032 (2) and 0·0140 (3) Å^2 parallel to and perpendicular to the basal plane, respectively. Values for the parallel vibrations of 0·0031 (6) and 0·0032 Å^2 were derived from temperature-dependent neutron measurements and a calculated phonon spectrum. The neutron measurements and the phonon spectrum both predict lower values [0·0090 (20) and 0·0098 Å^2] for the out-of-plane vibrations. This small discrepancy may be caused by small changes in the core atomic scattering factors from the free-atom values or by a deficiency in the phonon-spectrum model.

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Introduction

Charge-density analysis, which uses least-squares-refinement techniques to describe nonspherical charge distributions, has the potential for yielding accurate thermal parameters from X-ray diffraction data. When free-atom scattering factors are used with conventional refinement techniques, the thermal parameters tend to compensate for the deficiencies in the assumed atomic charge distributions. To test the ability of charge-density-analysis techniques to separate thermal-smearing effects from the nonspherical charge distributions, the thermal parameters from a recent X-ray diffraction study on graphite (Chen, Trucano & Stewart, 1977) were analyzed. These thermal parameters were then compared with other values obtained from a temperature-dependent neutron diffraction study (Ludsteck, 1972) and from a phonon spectrum which was calculated using specific-heat data (Young & Koppel, 1965). These comparisons establish better estimates of the graphite thermal parameters and indicate the extent to which basic assumptions of the charge-density analysis are met.

Review of relevant results

(*a*) *X-ray data*

The graphite data of Chen, Trucano & Stewart (1977), which extended to $\sin\theta/\lambda = 1{\cdot}2$ Å^{-1}, were obtained from small, natural single crystals. Neutron diffraction data on another crystal from the same source gave thermal parameters which were consistent with the X-ray results but which had higher estimated errors (Trucano & Chen, 1975). The X-ray thermal parameters had low estimated standard deviations. The common problem of high correlations between thermal parameters, scale, monopole populations, and/or radial function parameters was not encountered due in large part to the highly anisotropic nature of the graphite thermal motion.

In the harmonic approximation there are two independent parameters needed to describe the motion of each of the two C atoms in the asymmetric unit. One parameter (U_{11}) describes the mean-square amplitude of vibration in a direction parallel to the basal plane, and the other (U_{33}) describes the mean-square amplitude in a direction perpendicular to the basal plane. Table 1 contains these values which were determined by a charge-density analysis containing monopole through hexadecapole deformations, a common radial function for both independent C atoms, and anisotropic extinction parameters (Chen, Trucano & Stewart, 1977).

The effects of X-ray extinction can be compensated for by the thermal parameters. The fact that there was no significant change in the thermal parameters derived with and without extinction corrections (see Table 1) indicates that the effects of thermal motion and extinction were properly accounted for.

All previous measurements of the thermal motion in graphite were made with the assumption that both C atoms in the asymmetric unit vibrate with the same mean-square amplitude. The result of Chen, Trucano & Stewart (1977) is a direct experimental confirmation that this assumption is justified.

Although the calculation of Debye temperatures to describe thermal motion in anisotropic crystals is not a rigorous procedure, theoretical and experimental results are often expressed in this form. Therefore, the Debye temperatures for isotropic motion with a mean-square amplitude equal to U_{11} and U_{33} are also given in Table 1. These Debye temperatures were obtained by solving the following equation for Θ (James, 1965):

$$8\pi^2 U_{ii} = (6h^2 T/mk\Theta^2)[\Phi(\Theta/T) + \Theta/4T] \qquad (1)$$

where h, m, and k are Planck's constant, the atomic mass, and the Boltzmann constant respectively. T is the absolute temperature and

$$\Phi(x) = x^{-1} \int_0^x \xi(\exp \xi - 1)^{-1}\, d\xi.$$

Table 1. *Mean-square amplitudes of vibration for graphite in directions parallel to* (U_{11}) *and perpendicular to* (U_{33}) *the basal plane*

Θ_{11} and Θ_{33} are Debye temperatures associated with these amplitudes and C(1) and C(2) refer to the two independent atoms in the graphite unit cell.

		U_{11}	Θ_{11}	U_{33}	Θ_{33}
Chen, Trucano & Stewart (1977) (no extinction correction)	C(1)	0·0030 (2) Å^2	1330 ± 60 K	0·0137 (4) Å^2	533 ± 8 K
	C(2)	0·0033 (2)	1240 ± 60	0·0138 (4)	531 ± 8
Chen, Trucano & Stewart (1977) (with extinction corrections)	C(1)	0·0030 (2)	1330 ± 60	0·0140 (3)	527 ± 6
	C(2)	0·0033 (1)	1240 ± 30	0·0140 (3)	527 ± 6
Ludsteck (1972)		0·0031 (6)	$1300 {}^{+210}_{-110}$	0·0090 (20)	$670 {}^{+100}_{-70}$
Young & Koppel (1965)		0·0032	1266	0·0098	642

(*b*) *Neutron data*

The most recent experimental determination of graphite thermal parameters, other than the X-ray study referred to above, is based on temperature-dependent neutron diffraction intensities from the 002 and 110 reflections of polycrystalline samples (Ludsteck, 1972). Data collected between 300 and 1150 K were analyzed by Ludsteck to give the Debye temperatures listed in Table 1, and the associated mean-square amplitudes were obtained from equation (1). The agreement between the X-ray and neutron determinations is good, especially for the in-plane vibrations. The X-ray U_{33} value is two standard deviations below the neutron value, a discrepancy which may or may not be considered significant.

(*c*) *Lattice-dynamical results*

Several models of the graphite vibrational spectrum have been constructed. The most relevant to the data discussed here is an extension of the theory developed by Yoshimori & Kitano (1956) to fit specific-heat data in the range 100–1000 K (Young & Koppel, 1965). Young & Koppel derived a phonon spectrum which has two parts: one describes vibrations in the basal plane and the other describes vibrations perpendicular to the basal plane. These frequency distributions can be used to derive mean-square displacements comparable to those measured in diffraction experiments using the relationship (Blackman, 1955)

$$8\pi^2 U_{ii} = \frac{(2h/m)\int \nu^{-1}F(\nu)[\frac{1}{2} + (\exp X - 1)^{-1}]\,\mathrm{d}\nu}{\int F(\nu)\,\mathrm{d}\nu}, \qquad (2)$$

where $X = h\nu/kT$. The results are listed in Table 1.[*] Note that the agreement for the three different determinations of U_{11} or Θ_{11} is extremely good. The lattice-dynamical result leads to a value of U_{33} which is low compared with the X-ray value and in agreement with the neutron value. Estimates of errors in the values derived from the phonon spectrum are difficult to make. It should be kept in mind that the phonon spectra were calculated by fitting specific-heat data. Therefore the higher frequencies are given a relatively greater weight than they would receive if the mean-square amplitudes were being matched. This is because the integration giving the specific heat contains a factor of ν^2 instead of the ν^{-1} found in the integration for U_{ii}. The Young & Koppel spectrum gives much higher specific-heat Debye temperatures, a situation similar to that found in Si and Ge (Batterman & Chipman, 1962).

Discussion

The relatively low value for the out-of-plane motion derived from the X-ray measurements prompts a close look at the assumptions that enter into charge-density analysis. There were indications of extinction in the graphite data, especially in the 00*l* reflections which are important in the determination of U_{33}. However, U_{33} did not change appreciably when the extinction corrections were applied, and if the corrected intensities were still affected by extinction one would expect the low-order reflections to have smaller intensities leading to a smaller value of U_{33}, not a higher one. Similar arguments may be made concerning the contribution of thermal diffuse scattering (TDS) to the observed X-ray intensities. No correction was made but TDS should be larger for higher-order reflections tending again to reduce the value of U_{33}.

The charge-density analysis was carried out with the assumption that all of the charge associated with each atom moves with that nucleus. This is probably not true for the charge that is far from the nuclear centers. However, this charge does not scatter appreciably except at low scattering angles. The charge, which is localized close to the nuclei and which does closely follow the nuclei, scatters over the whole range of scattering angles. Because the scattering at higher angles is the dominant factor in determining the thermal parameters, it is unlikely that this assumption will affect the derived numbers.

Stewart (1973) showed that the thermal parameters are very sensitive to the assumed model for the core charge density. Chen, Trucano & Stewart (1977) assumed a $1s^2$ core for the C atoms and used Clementi (1965) atomic orbitals. Stewart's (1973) analysis of the thermal motion of C atoms in diamond showed that these wave functions for the core led to high estimates of the thermal parameters compared to the lattice-dynamical calculation. The graphite comparison shows a small discrepancy in the same direction and supports Stewart's conclusion that Hartree–Fock core scattering factors are insufficient to describe the C atom's core density.

To summarize the results of this comparison of several determinations of thermal parameters in graphite: (1) there is gratifying agreement among the values based on X-ray charge-density analysis, neutron temperature-dependent measurements, and the results inferred from a calculated phonon spectrum; (2) charge-density analysis can separate the effects of

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[*] Ludsteck (1972) also derived values for Θ_{11} and Θ_{33} from Young & Koppel's spectra. However, the value he quotes for Θ_{11} is 15% higher than the value given in Table 1. Ludsteck's value for Θ_{33} is in good agreement with the Table 1 value. The authors divided the spectra, Fig. 5 of Young & Koppel (1965), into 125 points along the abscissa and read the ordinates on a vernier which allowed a precision of 0·3% of the maximum ordinate. The values were numerically integrated and yielded a normalization that was within 1% of that used by Young and Koppel. The integrations for U_{11} and U_{33} may involve somewhat larger errors since all frequencies do not receive equal weight. However, the discrepancy with Ludsteck's value of Θ_{11} cannot be explained unless there was an error or less rigor in his integration of the phonon spectrum.

thermal smearing from those of nonspherical charge distribution even when the X-ray data contain effects due to extinction; (3) there is a small discrepancy between the X-ray results and the parameters calculated from the phonon spectra. This discrepancy may indicate that the C atom cores may not be adequately described by Hartree–Fock core scattering factors or that the model used to derive the graphite phonon spectrum is deficient.

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Deux Nouvelles Structures Polytypiques dans le Système Titane–Soufre: 16*H* et 18*H*

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The structures of two recently discovered polytypes of titanium sulphide have been determined. The structure of 18*H*, mainly built on a stacking sequence similar to that of 8*H* (3212), confirms the formation mechanism formerly suggested for $TiS_{1.7}$ hexagonal polytypes. In the same way, the stacking sequence of 16*H* provides some evidence of a 4*H* → 12*H* transformation producing rhombohedral polytypes. The experimental data supporting these conclusions are presented in this paper.

Introduction

Un mécanisme de formation expliquant l'existence des structures polytypiques observées dans $TiS_{1,7}$ a été récemment proposé (Legendre, Moret, Tronc & Huber, 1975*b*; Legendre & Huber, 1977). Comme dans le cas de ZnS (Alexander, Kalman, Mardix & Steinberger, 1970) c'est l'interaction de fautes d'empilement avec les dislocations vis présentes dans les cristaux qui entraîne l'apparition de ces structures. Ces dernières sont constituées par un empilement compact d'atomes de soufre dont les sites octaédriques sont occupés par les atomes métalliques. Une couche de titane est alternativement pleine ou partiellement remplie afin de respecter la stoechiométrie du composé.

La séquence d'empilement des couches de soufre est caractéristique d'un polytype et impose (à une translation près) la position des couches métalliques. La connaissance des structures d'un nombre croissant de polytypes de sulfure de titane revêt une importance particulière dans la mesure où chacun de ces renseignements expérimentaux sert de test à la validité du mécanisme qui a été proposé.

Ainsi, comme on pourra le constater dans la suite de cet article, la connaissance des structures 16*H* et 18*H* apporte une confirmation supplémentaire à ce mode de formation. De plus, l'étude structurale détaillée du cristal dans lequel est situé 16*H* nous a permis d'entrevoir l'existence d'une transformation de phase qui serait la cause fondamentale de l'apparition des polytypes rhomboédriques.

Structure 18*H*

Cette structure dont l'existence a été déjà rapportée (Legendre & Huber, 1977) a été observée dans deux cristaux à symétrie hexagonale allongés selon **c** et dont la structure de base est 2*H*. Ils sont issus d'une ampoule de préparation chauffée pendant deux mois à la température de 920 °C. La composition du mélange initial était $TiS_{1,7}$. L'étude structurale systématique d'un