Le cation Ba(3), lui, s'entoure d'un tétradécaèdre irrégulier de neuf atomes. Les polyèdres de coordination du baryum ont été définis par le fait que les écarts entre les distances Ba—O voisines ne dépassent jamais 0,15 Å.

La Fig. 3 représente, en projection sur le plan *ab*, les cycles approximativement horizontaux et carrés de quatre polyèdres de coordination du baryum que l'on rencontre dans la structure. Ces groupes, de formule Ba_4O_{26}, sont constitués de deux dodécaèdres $Ba(1)O_8$ et $Ba(2)O_8$ partageant respectivement deux arêtes O(*E*12)–O(*E*42) et deux arêtes O(*E*21)–O(*E*31) avec deux tétradécaèdres $Ba(3)O_9$. Chaque polyèdre $Ba(3)O_9$ partage également son arête O(*E*41)—O(*E*41)' avec son centrosymétrique immédiatement voisin, liant ainsi le groupe Ba_4O_{26} avec un autre groupe voisin. Chaque cycle Ba_4O_{26} peut donc être considéré comme le maillon d'une chaîne infinie se développant dans la direction **a** – **c**.

Le Tableau 2 donne les principales distances interatomiques et angles des liaisons dans les deux types d'anion Cr_2O_7, ainsi que les distances baryum—oxygène.

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Laevorotatory $Bi_{12}GeO_{20}$: Remeasurement of the Structure

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Abstract. $Bi_{12}GeO_{20}$, cubic, *I*23, $a = 10{\cdot}14540\,(8)$ Å corrected to 298·2 K, for $\lambda(\mathrm{Cu}\,K\alpha_1) = 1{\cdot}540598$ Å; $Z = 2$, $D_m = 9{\cdot}232\,(3)$, $D_x = 9{\cdot}222$ Mg m^{-3}.The crystal source was a commercially grown laevorotatory boule. Least-squares refinement resulted in $R = 0{\cdot}0275$ for 1396 independent structure factors. The determination is drawn from the same normal population as that of Abrahams, Jamieson & Bernstein [*J. Chem. Phys.* (1967). **47**, 4034–4041] but is of higher precision. Interatomic Bi—O distances, based on the weighted mean atomic coordinates from both determinations, are within 0·017 Å of the earlier values. The present Ge—O distance is 1·758 (5) Å, the previous value was 1·717 (28) Å. The atomic arrangement is shown, from the anomalous-scattering intensity differences, to have opposite chirality to that of the crystal studied earlier.

Introduction. The crystal structure of $Bi_{12}GeO_{20}$ was determined by Abrahams, Jamieson & Bernstein (1967), hereafter AJB. The sense of the piezoelectric polarization induced by applying tensile stress along a body diagonal of the body-centered cubic unit cell was shown by AJB to be such that the oxygen tetrahedron about each Ge atom on that diagonal is oriented with the apex pointing toward the positively polarized face normal to the stress. This is the result expected on the basis of a point-charge model (Abrahams, 1972). Interest in relating the chirality of enantiomorphous crystals (*i.e.* the handedness of atomic arrangement, in the absence of dissymmetric molecules) to the sense of rotation of plane-polarized light passing through the crystal, has recently increased (Abrahams, Glass & Nassau, 1977; Abrahams, Svensson & Tanguay, 1979). $Bi_{12}GeO_{20}$ is optically active, with a measured optical rotation that ranges from 124° mm^{-1} at 0·375 μm to 20° mm^{-1} at 0·64 μm (Hennessey & Vedam, 1975). The optical rotation sense of the AJB crystal had not been measured and hence could not be related to the absolute determination of crystal chirality. This paper reports the chirality of a laevorotatory crystal of $Bi_{12}GeO_{20}$ and compares the structural results with those of AJB.

A sphere of $Bi_{12}GeO_{20}$ of radius 0·1340 (15) mm was ground from a crystal slice, cut and optically polished by Dr A. R. Tanguay, who determined it to be uniformly laevorotatory. The slice was taken from a boule grown at Crystal Technology, Inc. All reflections within a hemisphere of reciprocal space of radius $(\sin\theta)/\lambda \leq 1{\cdot}15$ Å^{-1} and bounded by $0 \leq h, |k|, |l| \leq 20$ were measured with an Enraf–Nonius CAD-4

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diffractometer controlled by a PDP 11/40-8e computer and Enraf–Nonius (1977) software. Pyrolytic graphite-monochromatized Mo $K\alpha$ radiation was used with an ω–2θ scan. The integrated intensities of 6595 reflections were measured and corrected for Lorentz, polarization and absorption effects ($\mu = 97{\cdot}3\ \mathrm{mm}^{-1}$, minimum and maximum transmission factors of 4·91 and 145·1 × 10^{-4}). Three standard reflections were redetermined following each 50th integrated intensity measurement. No significant trends in the magnitudes of the standard reflections were noted, the standard deviation of the mean being 0·95%. Equivalent reflections were averaged, resulting in 2082 independent $F_{\rm meas}$ of the form *hkl* and $hk\bar{l}$. Standard deviations were derived as given by Abrahams, Bernstein & Keve (1971) with constants of 38·0 and 7·8 × $10^{-4}(F_{\rm meas})^4$. A total of 1396 of the independent $F_{\rm meas}$ had $F^2_{\rm meas} > 3\sigma F^2_{\rm meas}$: the remainder were regarded as unobserved and were not used in the following analysis.* A correction for extinction (Coppens & Hamilton, 1970) was made: the coefficient $g = 2{\cdot}7\ (5) \times 10^2$ is small, the maximum correction being 9·9% for $F(310)$. The systematic absences have been given previously by AJB.

Agreement indicators for each of the models refined, based on atomic scattering factors for neutral Bi, Ge and O taken from *International Tables for X-ray Crystallography* (1974) and obtained using *ORFLS* (Busing, Martin & Levy, 1973), are presented in Table 1. The hypotheses that the thermal vibrations in $Bi_{12}GeO_{20}$ are isotropic rather than anisotropic, and that the model corresponding to the *xyz* configuration fits the right-handed experimental data better than the $\bar{x}\bar{y}\bar{z}$ configuration, can both be tested by use of Hamilton's (1965) $\mathcal{R}$ ratio. The theoretical ratios are 1·011 and 1·003, the values from Table 1 are 1·517 and 1·307 respectively, hence both hypotheses can be rejected safely at the half-percent significance level. The coordinates in Table 2 are enantiomorphic to those found by AJB, hence it may be deduced that the AJB crystal was dextrorotatory.

Table 1. *Structural refinement indicators for laevorotatory* $Bi_{12}GeO_{20}$

Definitions of *R*, *wR* and *S* are given by AJB. All models are corrected for extinction and one scale factor is varied.

Parameters varied	Number of variables	R	wR	S
xyz, B	16	0·0452	0·0564	1·097
$\bar{x}\bar{y}\bar{z}, B$	16	0·0396	0·0490	0·955
xyz, β_{ij}	28	0·0350	0·0422	0·825
$\bar{x}\bar{y}\bar{z}, \beta_{ij}$	28	0·0275	0·0323	0·632

Table 2. *Atomic position coordinates of laevorotatory* $Bi_{12}GeO_{20}$ *at* 298 K

All coordinates, except for those of Ge, have had unity added to eliminate minus signs. The occupancy factor for Ge is 0·87 (2) per $Bi_{12}GeO_{20}$.

	x	y	z	B (Å^2)
Bi	0·17587 (2)	0·31832 (3)	0·01600 (2)	0·652 (5)
Ge	0	0	0	0·18 (6)
O(1)	0·1349 (5)	0·2514 (5)	0·4866 (6)	0·94 (8)
O(2)	0·1953 (7)	0·1953	0·1953	0·86 (14)
O(3)	0·8998 (6)	0·8998	0·8998	1·04 (15)

Discussion. The present diffraction results may be compared with those of AJB by use of normal probability analysis (Abrahams & Keve, 1971). Fig. 1 shows the δm plot based on 605 pairs of $F_{\rm meas}$ common to the two scaled sets of measured structure factors. Apart from a total of 26 terms in the extrema, derived from weak $F_{\rm meas}$, the plot is close to linear with zero intercept and slope of 0·991. Both sets of $F_{\rm meas}$ and $\sigma F_{\rm meas}$ hence have a normal random distribution, with well-assigned $\sigma F_{\rm meas}$. A δp plot, based on the 25 independent parameter values given in Tables 2 and 4* and those obtained under identical refinement conditions using the AJB set of 631 $F_{\rm meas}$ (Tables 5 and 6),* contains six terms that deviate severely from linearity, particularly the three β_{ii} terms for Bi. An additional comparison was made by using parameter values derived from the two sets of $F_{\rm meas}$ common to

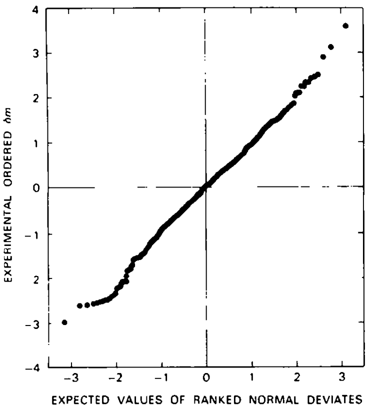

Fig. 1. Normal probability plot of 605 δm order statistics based on structure factors common to the AJB set (1) and the present set (2), where $\delta m = |F(\text{set 1}) - kF(\text{set 2})|/|\sigma^2 F(\text{set 1}) + k^2\sigma^2 F(\text{set 2})|^{1/2}$, against the expected normal order quantiles.

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* Lists of structure factors and Tables 4, 5, 6, 7, 8 and 9 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34506 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

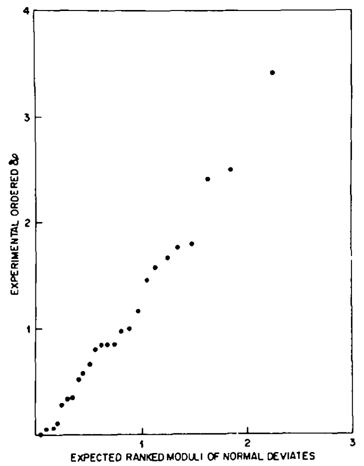

Fig. 2. Half-normal probability plot of 25 δp order statistics, with the thermal parameters derived from the CAD-4 measurements multiplied by 1·45, against the expected ranked moduli of the normal deviates, where $\delta p = |p(\text{set }1) - p(\text{set }2)|/|\sigma^2 p(\text{set }1) + \sigma^2 p(\text{set }2)|^{1/2}$. The parameters in sets 1 and 2 are derived from the structure factor sets of Fig. 1.

the δm plot. The resulting δp plot was more nearly linear, but the three Bi β_{ii} terms continued to deviate sharply from linearity. The values of the thermal parameters derived from the 605 CAD-4 measurements were about 31% smaller than those of AJB using PEXRAD. Attributing this reduction to a combination of increased thermal diffuse and multiple scattering components in the present experiment, associated with the different technique and higher crystal perfection, all thermal parameters from the CAD-4 measurements were multiplied by the factor 1·45. The δp plot based on these corrected data, shown in Fig. 2, becomes nearly linear with a slope of 1·35. No significant differences occur between the parameter values obtained with all 1396 CAD-4 F_{meas}, and those obtained with the 605 terms used in the δm plot.

The standard deviations estimated in Tables 2 and 4 are hence too low by about a factor of 1·4. The inference from Figs. 1 and 2 that the two independent structural determinations give results drawn from the same normal population indicates that the weighted means of both sets of parameters are more representative of $Bi_{12}GeO_{20}$ than either taken separately. The resulting weighted mean position coordinates are given in Table 3; the weighted mean anisotropic temperature coefficients are in Table 7.* The mean position coordinates are close to the values in Table 2 since these have standard deviations generally less than 25% those of AJB. The standard deviations in Tables 3, 7, 8 and 9* have been increased by the factor 1·4, taken from Fig. 2.

Table 3. *Weighted mean atomic position coordinates of laevorotatory* $Bi_{12}GeO_{20}$ *at* 298 K

Based on coordinates in Tables 2 and 5, $\hat{x}_i = [x_i(1)/\sigma^2 x_i(1) + x_i(2)/\sigma^2 x_i(2)]/[1/\sigma^2 x_i(1) + 1/\sigma^2 x_i(2)]$, where $x_i(1)$ is the ith coordinate obtained with AJB and $x_i(2)$ is the corresponding coordinate obtained with the CAD-4 structure factor refinement. Standard deviations are multiplied by 1·4 (see text).

	$\hat{x}$	$\hat{y}$	$\hat{z}$
Bi	0·17587 (3)	0·31833 (3)	0·01598 (3)
Ge	0	0	0
O(1)	0·1348 (7)	0·2515 (7)	0·4867 (8)
O(2)	0·1957 (9)	0·1957	0·1957
O(3)	0·8999 (8)	0·8999	0·8999

Interatomic distances in $Bi_{12}GeO_{20}$ based on the weighted mean coordinates of Table 3 are given in Table 8,* and interatomic angles are in Table 9.* These values were calculated using *ORFFE* 3 (Busing, Martin & Levy, 1973). Bi—O distances about the seven-coordinated Bi atom range from 2·069 Å for the short apical Bi—O bond to 3·078 and 3·186 Å for the lone-pair coordinated O atoms: these distances are within 0·017 Å of AJB's values. The Ge—O distance of 1·758 Å is closer to the value of 1·77 Å predicted on the basis of Shannon's (1976) Ge(IV)$^{4+}$ and O(IV)$^{2-}$ crystal radii than is the 1·717 Å value of AJB. The mean Ge—O distance in Na_2GeO_3 is 1·756 Å (Cruickshank, Kálmán & Stephens, 1978), and in quartz-like GeO_2 it is 1·740 (2) Å (Smith & Isaacs, 1964).

It is a pleasure to thank Dr A. R. Tanguay Jr for providing the slice of laevorotatory $Bi_{12}GeO_{20}$: one of us (CS) wishes to thank the Swedish Natural Sciences Research Council, the Swedish Directory for Technical Development and the Fulbright Exchange Program for grants.

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* See deposition footnote.

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Structure de l'Orthothiogermanate d'Europium

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Abstract. Eu_2GeS_4, monoclinic, $P2_1$, $a = 6{\cdot}638$ (1), $b = 8{\cdot}146$ (1), $c = 6{\cdot}672$ (1) Å, $\gamma = 108{\cdot}20$ (2)°, $Z = 2$, $d_m = 5{\cdot}2$, $d_x = 4{\cdot}89$ Mg m^{-3}, $\mu = 20{\cdot}9$ mm^{-1} (Mo $K\alpha$). The final R value was 0·032 for 1214 independent reflections. In this compound, the thiogermanate ion is formed by a GeS_4 tetrahedron and the Eu atoms are surrounded by seven S atoms.

Introduction. Le composé Eu_2GeS_4 a été obtenu par union du sulfure d'europium EuS et de la variété vitreuse du sulfure de germanium GeS_2. La synthèse a été réalisée sous vide en ampoule de silice. Le traitement thermique prolongé pendant 24 heures à une température de 1223 K est suivi d'un lent refroidissement (Barnier & Guittard, 1978).

Du produit ainsi obtenu, nous avons isolé un monocristal de couleur rouge orangé, ayant approximativement la forme d'un parallélépipède oblique de dimensions: 50 × 90 × 110 µm.

Une étude préliminaire montre que le cristal choisi appartient au système monoclinique. Sa direction d'allongement se révèle être l'axe binaire. Les extinctions systématiques ne sont observées que pour les réflexions $0k0$, et selon la condition $k = 2n + 1$. Il s'ensuit que les deux groupes d'espace possibles sont: $P2_1$ et $P2_1/m$. 1611 réflexions indépendantes ont été mesurées à l'aide d'un diffractomètre à quatre cercles CAD-4 Nonius, en utilisant un balayage en θ–2θ d'amplitude $s(°) = 0{,}80 + 0{,}35$ tg θ ($1° \leq \theta \leq 35°$). Les intensités ont été corrigées des facteurs de Lorentz et de polarisation.

La distribution statistique des facteurs de structure normalisés présente les caractéristiques d'une structure centrosymétrique.

Compte-tenu de ces résultats et d'une isotypie vraisemblable avec Sr_2GeS_4, suggérée par la similitude des diffractogrammes de poudre (Michelet, 1972), nous avons fait une première tentative pour déterminer la structure de Eu_2GeS_4 en adoptant le groupe $P2_1/m$ et les positions atomiques de Sr_2GeS_4 (Ribes, Philippot & Maurin, 1970). L'affinement des positions atomiques par la méthode des moindres carrés a été réalisé à l'aide du programme de Busing, Martin & Levy (1962). Les facteurs de diffusion utilisés sont ceux donnés dans *International Tables for X-ray Crystallography* (1974).

Une correction d'absorption, à partir d'un modèle cristallin parallélépipédique de dimensions 50 × 90 × 110 µm, a été effectuée à l'aide du programme de J. A. Ibers d'après la méthode analytique décrite par de Meulenaer & Tompa (1965).

Toutes les réflexions ont été corrigées de l'extinction secondaire isotrope suivant la méthode de Becker & Coppens (1974).

Tableau 1. *Coordonnées atomiques relatives avec leurs écarts-type et coefficients d'agitation thermique isotrope* (Å^2)

	x	y	z	$B_{\text{éq}}$
Eu(1)	0,71839 (9)	0,05209 (8)	$\frac{1}{4}$	1,22 (3)
Eu(2)	0,76732 (11)	0,56775 (9)	0,2478 (5)	1,29 (3)
Ge	0,2731 (2)	0,2001 (2)	0,2657 (6)	0,75 (5)
S(1)	0,0968 (7)	0,9233 (5)	0,2889 (9)	1,54 (2)
S(2)	0,0783 (6)	0,3738 (5)	0,2802 (14)	1,71 (2)
S(3)	0,4846 (11)	0,2576 (12)	0,0052 (10)	1,03 (2)
S(4)	0,4946 (10)	0,7359 (12)	0,0128 (9)	0,96 (2)

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