Table 3. Cs_3CoCl_5. *Interatomic distances less than* 4 Å

Reference atom	Nearest neighbours		
Cs (1)	8 Cl (2) at	3·820 Å	(3·67)
	2 Cl (1)	3·639	(3·62)
Cs (2)	2 Cl (1)	3·440	(3·42)
	2 Cl (2)	3·433	(3·39)
	4 Cl (2)	3·622	(3·85)
Cl (1)	2 Cs (1)	3·639	(3·67)
	4 Cs (2)	3·440	(3·42)
Cl (2)	Co (1)	2·252	(2·34)
	2 Cs (1)	3·820	(3·67)
	1 Cs (2)	3·433	(3·39)
	2 Cs (2)	3·622	(3·85)
	1 Cl (2)	3·982	(3·45)

Kruh, 1952) demonstrate a larger distortion than is found in any tetrahedral cobaltous complex.

It seems more reasonable therefore to associate the distortions in the cobalt complexes with crystal packing effects. In Cs_3CoCl_5, the tetrahedra of $[CoCl_4]^{2-}$ ions arranged about the 001 plane interact more strongly in the *a* (*b*) direction along which the flattening of the tetrahedron is observed (Fig. 2). The chlorine–chlorine distance is 3·892 Å and our magnetic data show that this interaction allows antiferromagnetic interaction between the cobalt ions in the (001) plane via a super-exchange mechanism. Similar close contacts are observed in Cs_2CoCl_4 and $K_2Co(CNS)_4.4H_2O$. While the distortions in the latter molecules are not simple axial ones, it seems generally true that the angular distortions can at least be qualitatively correlated with specific steric effects in the crystal.

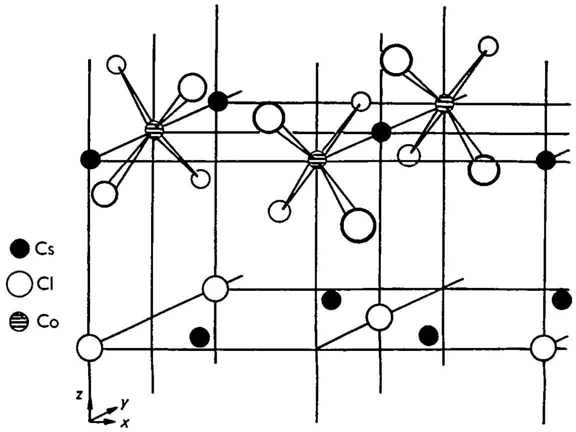

Fig. 2. Cs_3CoCl_5. The crystal structure.

We are grateful to Drs J. S. Rollett and R. Sparks for copies of their programs for the University of London Mercury computer. One of us (M. G.) is in receipt of a D.S.I.R. Research Studentship.

References

Figgis, B. N., Gerloch, M. & Mason, R. (1964). *Proc. Roy. Soc.* A. In the press.

Helmholz, L. & Kruh, R. F. (1952). *J. Amer. Chem. Soc.* **74**, 1176.

Jeffrey, J. W. Personal communication.

Porai-Koshits, M. A. (1954). *Trudy Inst. Krist., Akad. Nauk SSSR.* **10**, 117.

Powell H. M. & Wells, A. F. (1953). *J. Chem. Soc.* p. 359.

Zdhandov, G. S. & Zvonkhova, Z. V. (1950). *Zhur. fiz. Khim.* **24**, 1339.

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The Use of Germanium Dendrites for the Monochromatization of X-rays

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Germanium dendrites have been found to be very suitable as monochromatizing plane or bent crystals owing to their remarkable elasticity and high perfection. Both experimental and theoretical comparison was made with quartz. The intensities of the monochromatized beams in the two crystals were comparable but owing to the fine polishing of the germanium dendrite the reflected intensity was almost doubled. Germanium dendrites are especially suitable as monochromators with variable curvature.

Introduction

Recently more and more attention has been drawn to artificially grown germanium and silicon crystals with a high degree of perfection. Their advantages as plane monochromators in X-ray spectroscopy has been proved in a series of papers (*e.g.* Drahokoupil & Fingerland, 1959; Bubáková, Drahokoupil & Fingerland, 1962). They have, however, one common disadvantage, namely that the preparation of the polished plate is expensive and laborious. When Andrle (1961) published his results on the preparation of perfect germanium dendrites the possibility of using germanium dendrites as monochromatizing bent crystals occurred to one of the present authors (A.F.). There are some general conditions required of a crystal used as an X-ray monochromator: (1) crystallographic perfection, (2) adequate intensity of the reflected X-ray beam, (3) elasticity, and (4) chemical stability. Properties (3) and (4) are obviously fulfilled in germanium dendrites; properties (1) and (2) were a matter for investigation.

Experimental

A. A transverse cut was made in the dendrite used and, after polishing and etching, a relief schematically drawn in Fig. 1 was observed. The dimensions of the cut were 7 × 0·4 mm. This cut was made at each end of the dendrite and the results were the same. The dendrite is composed of three parts: part I is limited on the outside by its natural mirror-like face, (111), and on the other side by a twinning plane along which it comes into contact with part II. This part widens in the middle (dendritic nucleus) and at each end of the transverse cut. In the narrowest part etch pits, the nature of which we did not study, could be observed. Part III joins part II along the second twinning plane and is also limited on the outside by a natural mirror-like plane, the indices of which are, in this orientation, $(\bar{1}\bar{1}\bar{1})$. All along the centre of the natural plane $(\bar{1}\bar{1}\bar{1})$ there is the so-called 'chorda'* consisting of a line of points.

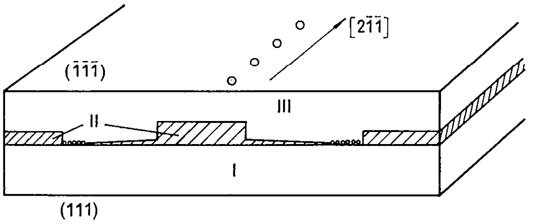

Fig. 1. A transverse cut of a dendrite (schematic). I, perfect side; II, middle layer; III, imperfect side.

From now on we shall refer to plane (111) as the 'perfect side' and to plane $(\bar{1}\bar{1}\bar{1})$ as the 'imperfect side' of the dendrite, in agreement with Vasilevskaja, Miseljuk & Fortunatova (1963).

B. On a three-crystal spectrometer (as used by Bubáková, Drahokoupil & Fingerland, 1961) the dendrite was measured on both sides. The measurements indicate that on the 'perfect side', the dendrite reflects as a highly perfect monocrystal, while on the imperfect side the result was not so satisfactory. The percentage reflexion (according to the definition used by Bubáková *et al.*, 1961) was found on the perfect side to be 84%, on the imperfect side 55%. Fig. 2 shows both diffraction curves; the theoretical curve for an ideal germanium crystal, taken from the paper by Bubáková *et al.* (1961), is indicated by the dotted line.

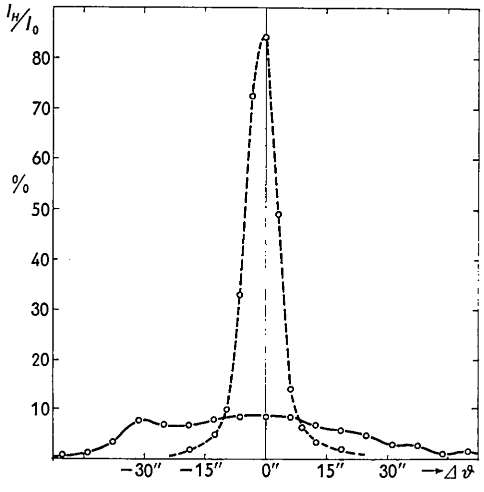

Fig. 3. A three-crystal rocking curve of quartz (full line) and of the perfect side of the germanium dendrite (dotted line).

C. In the same way, the quartz crystal used in the monochromator was also measured. Fig. 3 indicates that the range of angles at which the crystal reflects is considerable, the percentage reflexion being about

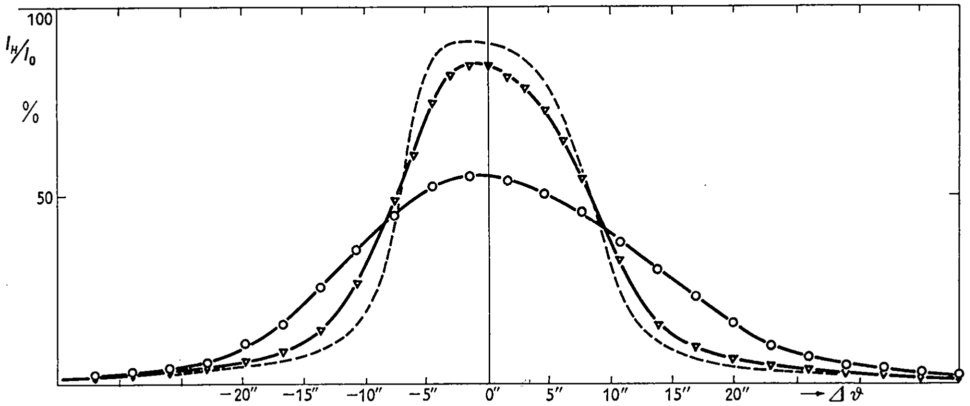

Fig. 2. A three-crystal rocking curve of a dendrite:
○ Imperfect side ▽ Perfect side – – – Theoretical curve for perfect crystals

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* This name has been adopted from the paper by Andrle (1961).

8%. The diffraction curve of the perfect side of the dendrite (dotted line) was simultaneously plotted in the same figure to facilitate comparison.

D. Finally, the crystal was fixed into a bent-crystal holder with a 600 mm diameter of curvature joined to a Guinier camera Ø 114 mm and a powder diffraction pattern of sodium chloride with Cu $K\alpha$ radiation was taken. The result was compared qualitatively with a pattern taken on the same sample with a quartz monochromator and then with a germanium dendrite which was finely polished with carborundum '800' powder. The conditions were kept constant during these three exposures, namely: 35 kV, 18 mA, exposure time 30 minutes. The measured integral intensity of the NaCl 200 line was then as follows: with dendrite 241, with quartz 225 and with polished dendrite 392.

Theoretical*

Owing to the difficulty of drawing theoretical conclusions on bent crystals, Ge and quartz were compared by using the integrated reflexions of plane crystals. The calculations were carried out according to the results published by Hirsch & Ramachandran (1950) and in a simplified form by Fingerland (1962). The integrated reflexion is given by the relation

$$\varrho = C\,.\,N|F'|R^y(g, k)/\sin 2\theta_B \tag{1}$$

where C is a constant which also includes the polarization factor, N is the number of elementary cells in 1 cm^3, $|F'|$ is the absolute value of the real part of the structure factor and θ_B is the Bragg angle. $R^y(g, k)$ in the dynamical case $\simeq \frac{8}{3}(1-2{\cdot}4|g|)$, in the kinematical case $\simeq \pi/4|g|$, $g \simeq -\frac{1}{2}(mc^2/e^2)(\mu_L/|F|\lambda N)$; and μ_L is the linear absorption coefficient.

Because the Bragg angles of both quartz (Q) and germanium crystals are practically the same we can write for the relation of integrated intensities

$$\frac{\varrho_{\text{Ge}}}{\varrho_{\text{Q}}} = \frac{N_{\text{Ge}}|F_{\text{Ge}}|R^y_{\text{Ge}}}{N_{\text{Q}}|F_{\text{Q}}|R^y_{\text{Q}}} = \eta\,.$$

In Table 1 the values used for the calculation are given. In this table d is the interplanar distance, S is the geometrical structure factor, f is the atomic factor. For purposes of estimation three out of four possible cases were evaluated:

$$\varrho_{\text{Ge}}\,(\text{dyn})/\varrho_{\text{Q}}\,(\text{dyn}) = \eta(d\mid d) \doteqdot 2{\cdot}7$$
$$\varrho_{\text{Ge}}\,(\text{dyn})/\varrho_{\text{Q}}\,(\text{kin}) = \eta(d\mid k) \doteqdot 0{\cdot}6$$
$$\varrho_{\text{Ge}}\,(\text{kin})/\varrho_{\text{Q}}\,(\text{kin}) = \eta(k\mid k) \doteqdot 3{\cdot}8$$

From the measured diffraction curves (Fig. 3) it is apparent that the first case ($\eta(d\mid d)$) can be eliminated because the quartz (which was used here) has a ϱ_{Q} much nearer to the kinematical value. It is therefore possible to suppose that in one case the germanium dendrite is practically perfect; in the case of polished dendrite the value R^y is in the range $(2{\cdot}32-14{\cdot}5)$, and in the case of quartz it is in the range $(2{\cdot}13-9{\cdot}4)$. If we choose in both cases the mean values ($R^y_{\text{Ge}} \sim 8$; $R_{\text{Q}} \sim 6$), we get $\eta(d\mid k) \sim 1$, $\eta(k\mid k) \doteqdot 3$.

Table 1. *Data used for evaluating* $\varrho_{\text{Ge}}/\varrho_{\text{Q}}$

Symbol	Ge (111)	Q (10$\bar{1}$1)
N $(=1/v)$	$1/180 \times 10^{24}$ cm^{-3}	$1/113 \times 10^{24}$ cm^{-3}
d	$3{\cdot}27 \times 10^{-8}$ cm	$3{\cdot}35 \times 10^{-8}$ cm
f	25·5	Si^{4+} 9·37 O^{2-} 6·35
S	$\sqrt{32}$	Si 2·356 O 2·193 *
$\lvert F\rvert$	145	36
μ_L	375	232
$\lvert g\rvert$	0·054	0·084
R^y dyn.	2·32	2·13
kin.	14·5	9·4

* According to Dr Čermák (private communication).

Discussion

When theoretical and experimental values are compared, it is apparent that the dendrite used diffracted as a highly perfect monocrystal, while ϱ for quartz seemed to be closer to the kinematic value. This is consistent with the measurements of integrated intensities of the NaCl 200 reflexion, because the relation of this intensity measured on germanium dendrite to that measured on quartz is $245/225 = 1{\cdot}1$ (theoretically $\doteqdot 1$); polished dendrite and quartz give the mean value $392/225 = 1{\cdot}8$ (theoretically $\doteqdot 3$). It should be noted that the conditions at which the powder diffraction patterns were obtained are only approximately the same: *viz.* the same 'load' on the X ray tube, the same diameter of curvature of the crystal, the same camera and sample, approximately the same diffraction angle of germanium and quartz and the same exposure time.

Conclusion

It has been shown that germanium dendrites are suitable crystals for X-ray monochromators because they are of outstanding perfection and they give a sufficiently intensive monochromatic beam, *i.e.* they possess all the properties mentioned in the introduction. Moreover, in view of the diamond structure of germanium and the use of the reflexion on the (111) plane the harmonic $\lambda/2$ does not occur and the high quality of the natural faces of the dendrite makes the delicate preparation of the crystal unneccesary. Thus their high degree of perfection renders them highly suitable as plane monochromators on the one hand,

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* The theory given in the paper by Hirsch & Ramachandran (1950) is valid only for crystals with a centre of symmetry, but it seems to us that for the strong 10$\bar{1}$1 reflexion of quartz we can use similar considerations.

while their great elasticity and flexibility makes them suitable as monochromatizing crystals with variable curvature.

Our thanks are due to Ct. Andrle of the VÚST A. S. Popova for the germanium dendrites and for discussions concerning them, Dr J. Drahokoupil for enabling us to make measurements on the three-crystal diffractometer, Ing. Hrubý and J. Kašpar for assistance in etching, Dr J. Čermák for supplying the theoretical values of quartz, and A. Dobrovodská and V. Šídová for their careful measurements.

References

ANDRLE, C. (1961). *Čes. Čas. Fys.* A11, p. 397; *IVth Conf. on Monocrystals*, Turnov.

BUBÁKOVÁ, R., DRAHOKOUPIL, J. & FINGERLAND, A. (1961). *Czech. J. Phys.* B **11**, 199.

BUBÁKOVÁ, R., DRAHOKOUPIL, J. & FINGERLAND, A. (1962). *Czech. J. Phys.* B **12**, 539, 765.

DRAHOKOUPIL, J. & FINGERLAND, A. (1959). *Conf. on X-ray Wavelength Problems*, Stockholm.

FINGERLAND, A. (1962). *Czech. J. Phys.* B **12**, 264.

HIRSCH, P. B. & RAMACHANDRAN, G. N. (1950). *Acta Cryst.* **3**, 187.

VASILEVSKAJA, V. N., MISELJUK, E. G. & FORTUNATOVA, N. N. (1963). *Fiz. Tverdovo Tela*, **5**, 52.

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The Crystal Structure of 15,15′-Dehydro-β-carotene[*]

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The crystal structure of 15,15′-dehydro-β-carotene, $C_{40}H_{54}$, at -20 °C has been determined by Fourier and least-squares analysis of complete three-dimensional intensity data from iron $K\alpha$ X-radiation. The crystals are monoclinic with space group $P2_1/c$; the unit cell, which contains two centrosymmetric molecules, has the dimensions $a=8{\cdot}14_5$, $b=31{\cdot}8_7$, $c=8{\cdot}46_5$ Å, $\beta=128°\ 18{\cdot}_8'$. With the exception of the *s-cis* orientation about the single bond from the chain to the cyclohexene ring the molecule is in the all-*trans* configuration. The central 18 carbon atoms of the structure are coplanar within 0·11 Å and deviations from planarity are consistent with the intermolecular arrangement. The single and double bonds of this highly conjugated linear molecule are distinctly different in length with average values of 1·455 and 1·345 Å, respectively. Despite rather large thermal motions of the molecule it has been possible to assign parameters to all of the hydrogen atoms, there being no evidence for the free rotation of the methyl groups.

Introduction

A previous communication (Sly, 1955) presented a projected structure of 15,15′-dehydro-β-carotene (DHC) (Fig. 1) along with preliminary three-dimensional coordinates and a brief description of the methods of analysis. The present paper on the structure of DHC reports the results of a three-dimensional refinement for this highly conjugated carotene using the previous data, which were collected at -20 °C. Since the refinement procedures used in this work are standard, this report will be concerned principally with the final results.

Solution and refinement

Sly (1955) reported the unit cell and space group given in the abstract above together with three-dimensional atomic coordinates. A three-dimensional Patterson function along with trial and error methods and structure factor maps had led to a well resolved and refined projection of the molecule along [101] onto (101). The preliminary three-dimensional atomic coordinates previously reported were obtained from the refined parameters of the projection with the aid of models and information from the three-dimensional Patterson function.

Since the earlier report the structure of DHC has been intensively refined. The steps of the refinement are outlined below, along with the reliability index, $R=(100)\ (\Sigma|\Delta F_{hkl}|)/(\Sigma|F_{o\,hkl}|)$, which resulted from

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