The Single-crystal Raman Spectra of Nearly Opaque Materials. Iron(III)

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A technique for studying orientation effects on nearly opaque single crystals with laser Raman spectroscopy is described in detail. The instrument used in these studies is a Spex monochromator. The scattering equations derived are applied to a study of iron(III) oxide and chromium(III) oxide.

IN 1965 Russell¹ reported the Raman spectrum of elemental silicon using 6328 Å helium-neon laser excitation. This investigation was thought to be the first time that Raman scattering had been observed in an opaque solid. Since that time the Raman spectra of many 'nearly opaque' materials have been published, including one of chromium(III) oxide.² By use of the Cary 81 on-axis illumination-observation system it is relatively easy to study highly absorbing materials such as K₂PdCl₄³ or V₂O₅.⁴ However, with materials that are both weak scatterers and also highly reflecting we have found it difficult to obtain high quality spectra with this sampling assembly.[†]

Oxide and Chromium(III) Oxide

It is clear that to obtain the Raman spectra of nearly opaque materials it will normally be necessary to use the same face of a crystal for illumination and observation. An obvious approach to the problem of high reflectivity materials is to work at the Brewster angle for illumination while collecting the Raman light perpendicular to this face or nearly so. For crystals of at least orthorhombic symmetry, Figure 1 is appropriate with the electric vector of the incident light in the plane of the paper and all the directions shown also lying in this plane. For accurate intensity measurements the axis of the collection system should ideally lie perpendicular to the plane of the crystal face (*i.e.* (i.e. $\theta = 90^{\circ}$). However, in view of difficulties associated with surface irregularity and optical anisotropy such refinement is usually unimportant, the conventional $(\delta = 90^{\circ})$ system being adequate.

For the example given in Figure 1 the plane of the paper is also a principal section of the triaxial refractive index ellipsoid known as the optical indicatrix. Any elliptic section of the indicatrix perpendicular to the plane of the paper will have the third indicatrix axis (that normal to the plane of the paper) as the major or the minor axis of that elliptic section. Thus for propa-

[†] It should be noted that our Cary 81 is not fitted with the most recent detection system.

J. P. Russell, Appl. Phys. Letters, 1965, 6, 223.

² D. A. Brown, D. Cunningham, and W. K. Glass, Spectrochim. Acta, 1968, 24A, 965.

³ I. R. Beattie and T. R. Gilson, Proc. Roy. Soc., 1968, A, 307,

^{407.} ⁴ I. R. Beattie and T. R. Gilson, J. Chem. Soc. (A), 1969,

gation of the laser light and observation of the Raman light by use of an analyser adjusted to pass the electric vector either in the plane of the paper (I_{\parallel}) or perpendicular to the plane of the paper (I_{\perp}) birefringence problems do not arise.* It is perhaps worth mentioning here that in our experience the results from this study are superior to those obtained on small, transparent, irregularly shaped crystals. Presumably this is due to the absence of internal reflections in the absorbing crystals.

In describing our experimental results we shall adopt the nomenclature I_{\parallel} and I_{\perp} as outlined above, together with the angle β which defines the relative orientations of the sample face and the crystallographic axes. It should be noted that I_{\parallel} means that the electric vector



FIGURE 1 The sampling arrangement used in this study for nearly opaque solids

of the incident light and the electric vector of the Raman light lie in the same *plane*. By contrast I_{\perp} is a 'true' perpendicular measurement.

Using the Raman intensity formula of Loudon 5 we write

$$I = K \{ \sum_{\sigma, \rho} e_{\sigma} R_{\sigma, \rho} f_{\rho} \}^2$$

where e_{σ} and f_{ρ} are respectively the direction cosines for the analyser pass direction and electric vector of the incident light; $R_{\sigma,\rho}$ is the σ,ρ th Raman tensor element where σ and ρ take the meanings x, y, z appropriately. For a general angle δ between laser and collection axes we find:

$$I_{\parallel} = K \{C_{xx}R_{xx} + C_{zz}R_{zz} + C_{xz}R_{xz}\}^2$$

with the assumption that $R_{xz} = R_{zx}$, where

$$C_{xx} = \frac{[nk\sin^2\beta - (k - nq)\sin\beta\cos\beta - q\cos^2\beta]}{n(1 + n^2)}$$

$$C_{zz} = \frac{1}{[nk\cos^2\beta - (k - nq)\sin\beta\cos\beta - q\sin^2\beta]/n(1 + n^2)}$$
$$C_{xz} = [(k - nq)\cos2\beta + (nk + q)\sin2\beta]/n(1 + n^2),$$

and $q = \sin \delta - n \cos \delta$

 $k^2 = n^2 (1 + n^2) - q^2$ where n = refractive index. However, if $R_{xz} \neq R_{zx}$ (as in electronic Raman spectra): $C'_{xz} = [-k \sin^2 \beta + (nk + q) \sin \beta \cos \beta - nq \cos^2 \beta]/n(1 + n^2)$

$$C'_{zx} = [k \cos^2 \beta + (nk + q) \sin \beta \cos \beta + nq \sin^2 \beta]/n(1 + n^2)$$

Here we adopt the convention that the second subscript refers to the exciting light, and the first to the Raman light. For $\delta = 90^{\circ}$, q = 1 and $k = (n^4 + n^2 - 1)^{\frac{1}{4}}$ whereas for collection of the Raman light strictly at 90° to the crystal surface q = 0 and $k = n(1 + n^2)^{\frac{1}{4}}$

where

$$C_{yx} = (n \sin \beta + \cos \beta)/(1 + n^2)^{\frac{1}{2}}$$
$$C_{yz} = (n \cos \beta - \sin \beta)/(1 + n^2)^{\frac{1}{2}}$$

 $\mathbf{I}_{\perp} = K \{ C_{yx} R_{yx} + C_{yz} R_{yz} \}^2$

It is clear from simple inspection of Figure 1 that I_{\perp} may be made a 'pure' measurement simply by arranging for the refracted laser ray to pass along the z axis (for R^2_{yx}) or the x axis (for R^2_{yz}). Analytically we see that from the above equations, $C_{yz} = 0$ when $n \cos \beta = \sin \beta$ *i.e.* tan $\beta = n$. Thus crystal faces cut with tan $\beta = n$ may be used to obtain the three (or six) off-diagonal Raman tensor components.

It might appear that the 'parallel' measurements would be much more difficult to interpret. However, if for example, the x axis of the crystal bisects the angle between the refracted laser ray and the (ideal) Raman collection direction in the crystal, then if the laser polarization direction becomes $\sigma = z - ax$. The product $\rho\sigma = (z + ax)(z - ax) = zz - a^2xx$ then contains *no* term in *xz*, so that I_{\parallel} may at least be restricted to diagonal tensor elements. Furthermore, if the refractive index is sufficiently large, the value of a^2 drops sufficiently that the term in *xx* may be ignored. This is particularly true for the 'ideal' arrangement with $\theta = 90^{\circ}$ (See Tables 1 and 2).

Analytically we see that $C_{xz} = 0$ when $\tan 2\beta = -(j - nq)/(jn + q)$ corresponding to the expected small negative value of β . It so happens that this 'ideal' value for β is approximately constant over the normal range of values of refractive index, when using the conventional ($\delta = 90^\circ$) arrangement (Table 1).

* We assume here that the normal laws of refraction also apply, thereby ignoring the detailed problems of the 'extraordinary rays.'

† The variation of n with wavelength is ignored for the purposes of this discussion. This is a highly questionable approach as for 'opaque' materials we are clearly working in the region of a strong absorption band where dispersion effects are at a maximum. However, we attempted to choose an exciting line near the region of minimum rather than the region of maximum absorption. This is also advisable in view of the assumption of 'normal' refraction.

⁵ R. Loudon, Adv. Physics, 1964, **13**, 423 (errata 1965, **14**, 621).

Notation for Spectra.—The usual notation for singlecrystal Raman spectra is not applicable to arbitrary propagation directions. Therefore we denote a particular spectrum as, e.g. for a crystal of refractive index 3, $I_{\parallel}; \quad \beta_{xz} = -6^{\circ} \quad 12'; \quad \delta = 90^{\circ}; \quad R^2_{zz} + 0.0023 R^2_{xx} - 12^{\circ}$ $0.10 R_{xx}R_{zz}$ (or simply ca. R^2_{zz})

cut at the prescribed angles, the choice of x and y may be quite arbitrary. The choice is also irrelevant for a trigonal crystal of any refractive index when β lies in the xy plane; thus both I_{\parallel} and I_{\perp} from a single face should be meaningful in that special case. A good check of this method of obtaining spectra, apart from

				TABLE 1				
.	Calculated	values for obs	ervations ad	cording to Fig	gure 1, (I_{\parallel} , β ic	leal) with $\delta =$	= 90°	
index index	β°	C^{2}_{xx}	C^{2}_{zz}	C^{2}_{xz}	$2C_{xx}C_{zz}$	$2C_{xx}C_{xz}$	$2C_{zz}C_{zz}$	f.no.
1.25	-4.338	$0.217 \\ 0.212$	1.00 1.00	0 0·0230	-0.932 - 0.898	0 0·00834	0 0·0495	∞ 1·6
1.50	-5.993	0·0759 0·0747	1·00 1·00	0 0·0120	-0.551 - 0.535	0 0·00400	0 0·0310	∞ 1·6
1.75	-6.638	0·0331 0·0329	1.00 1.00	0 0·00778	-0.364 - 0.355	0 0·00274	0 0·0214	∞ 1·6
$2 \cdot 00$	-6.822	0·0166 0·0166	1.00 1.00	0 0·00559	$-0.258 \\ -0.252$	0 0·00200	0 0·0156	∞ 1·6
$2 \cdot 25$	-6.782	0·00914 0·00920	1.00 1.00	0 0·00426	-0.191 - 0.188	0 0·00151	0 0·0118	∞ 1·6
2.50	6.629	0·00541 0·00547	1.00 1.00	0 0·00339	-0.147 - 0.145	0 0·00116	0 0·00923	∞ 1·6
2.75	-6.422	0·00338 0·00344	1.00 1.00	0 0·00277	-0.116 - 0.115	0 0·000905	0 0·00 739	∞ 1·6
3.00	-6.192	0·00222 0·00226	1.00 1.00	0 0·00231	-0.0942 - 0.0929	0 0·000718	0 0·00604	∞ 1·6
3.25	-5.956	$0.00151 \\ 0.00155$	1.00 1.00	0 0·00196	-0.0777 - 0.0767	0 0·000577	0 0·00501	∞ 1·6
3.50	-5.722	0·00106 0·00109	1.00 1.00	0 0·00167	-0.0651 -0.0643	0 0·000471	0 0·00422	∞ 1·6

TABLE 2

Calculated values for abservations according to Figure 1, (I_{\parallel} , β ideal) with $\theta = 90^{\circ}$

Retractive								
index	β°	C^{2}_{xx}	C^{2}_{zz}	C^{2}_{xx}	$2C_{xx}C_{zz}$	$2C_{xx}C_{xz}$	$2C_{zz}C_{xz}$	f.no.
1.25	-19.330	0·0151 0·0168	1·00 1·00	0 0·0170	-0.246 - 0.242	0 0·0110	0 0·0110	∞ 1.6
1.50	-16.845	0·00840 0·00925	1.00 1.00	0 0·0111	-0.183 - 0.181	0 0·00616	0 0·00616	$\infty 1 \cdot 6$
1.75	-14.872	0·00487 0·00545	1.00 1.00	0 0·00783	-0.141 - 0.140	0 0·00388	0 0·00388	$\stackrel{\infty}{1\cdot 6}$
2.00	-13.583	0·00311 0·00340	1.00 1.00	0 0·00582	-0.111 - 0.111	0 0·00260	0 0·00260	∞ 1·6
2.25	-11.981	0·00203 0·00221	1·00 1·00	0 0·00450	-0.0901 -0.0897	0 0·00183	0 0·00183	∞ 1·6
2.50	-10.901	0·00138 0·00150	1.00 1.00	0 0·00359	-0.0742 - 0.0739	0 0·00133	0 0·00133	$\infty 1.6$
2.75	-9.992	0·000963 0·00105	1.00 1.00	0 0·00293	-0.0621 -0.0619	0 0·00100	0 0·00100	$\infty 1 \cdot 6$
3.00	-9.217	0·000693 0·000754	1.00 1.00	0 0·00244	-0.0527 -0.0525	0 0·000770	0 0·000770	∞ 1·6
3.25	-8.551	0·000511 0·000556	1.00 1.00	0 0·00206	-0.0452 - 0.0451	0 0·000606	0 0·000606	$\infty 1 \cdot 6$
3.50	-7.973	0·000385 0·000418	1.00 1.00	0 0·00177	-0.0392 - 0.0392	0 0·000485	0 0·000485	∞ 1•6

Normally, of course, such great accuracy in the determination of β would be neither necessary nor possible.

Application to Trigonal Crystals.—Provided only that cross terms $C_{ij}C_{kl}$ may be kept down to a reasonably low value, the directions chosen for x and y in the plane perpendicular to the unique axis are irrelevant for trigonal crystals. Thus for crystals ⁶ such as α -Fe₂O₃ $(n \ ca. 3)$ and Cr_2O_3 $(n \ ca. 2.5)$, provided that faces are the obvious overlap obtainable between some measurements, lies in the R^2_{xx} and R^2_{xy} measurements. These should be identical for e_g bands (D_{3d} space group), with the xx spectrum showing, in addition, xx active a_q bands. In order to obtain as many checks as possible, five faces were cut on a crystal of Fe_2O_3 , resulting in six acceptable spectra. The results are shown in Figure 2

⁶ R. E. Newnham and Y. M. DeHaan, Z. Krist., 1962, 117, 235.



				1	004	0 11	CAUI	lau	on)		
(a)	I	β_{xx}	≈	-7°	ca.	R^{2}_{zz}	slit	2.7	cm1	sensitivity	$\times 1$
(b)								$5 \cdot 3$	cm1	-	imes 2.5
(c)	IL	βxy			ca.	R^2_{yz}		2.7	cm1		$\times 4$
(d)						-		$5 \cdot 3$	cm1		$\times 7$
(e)	I_{\perp}	β_{xx}	≈	-18°	ca.	R^{2}_{zy}		$5 \cdot 3$	cm1		$ imes 2 \cdot 5$
(f)						-		2.7	cm1		$\times 10$
(g)	I_{\perp}	β_{sx}	≈	-18°	ca.	R^{2}_{xy}		5.3	cm1		imes 7.5
(h)	I	β _{xy}			ca.	R^2_{yy}		5.3	cm1		imes 5
(i)	II:	β_{zx}	≈	-7°	ca.	\mathbf{R}^{2}_{xx}		$5 \cdot 3$	cm1		×4

(see also Table 3). For Cr_2O_3 less reliable orientation was available, and three faces were used to provide four 'acceptable' spectra, whilst an impure zz measurement off one of these faces was accepted as adequate for

			TABLE 3	3				
Observed	single	crystal	Raman	freque	encies	and	relati	ive
inten: 6328	sities fo Å	or α-Fe ₂	O_3 (not o	cooled)	with	excit	ation	at

(cm1)	xx-yy	22	xy	xz-yz	
226	0	100	0	~1	a_{1a}
245	5	0	5	0	ea
293	\mathbf{sh}	0	\mathbf{sh}	45	eg
298	8	0	8	\mathbf{sh}	e_q
413	19	0	19	1.5	ea
500	3	6	0	0	a 19
612	8	0	8	2	eg

TABLE 4

Observed single crystal Raman frequencies and relative intensities for $\rm Cr_2O_3$ (not cooled) with excitation at 5145 Å

xx–yy	22	xy	xz–yz
6	6	3*	0
2	0	2	7
1	0	1	0
0	0	0	2
100	100	2	1
5	0	7	4
	xx-yy 6 2 1 0 100 5	$\begin{array}{cccc} xx - yy & zz \\ 6 & 6 \\ 2 & 0 \\ 1 & 0 \\ 0 & 0 \\ 100 & 100 \\ 5 & 0 \end{array}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

* Much reduced on cooling.

assignment (Figure 3 and Table 4). Any details appearing in the figures but not the tables, are due to spurious lines (either from laser background emission or grating ghosts). The intensity of these features depends critically on the diffuse scattering, and hence the optical quality, of the surface under examination.

In the case of the spectra of α -Fe₂O₃ only one case departs significantly from the ideal, that is R^2_{xx} as obtained from I_{\parallel} , β_{zx} ca. -7° . In order to allow for the approximate value of β , the angle of incidence was allowed to assume a range of values close to the strict Brewster condition (Figure 4). Clearly, even the best of these spectra does not give the doublet envelope the same shape as that obtained from I_{\parallel} , β_{xy} (R^2_{yy}) or I_{\perp} , β_{zx} ca. -18° (R^2_{xy}). The latter two spectra are however closely similar apart from the presence of $v_1(a_{1g})$ in xxas required. In the anomalous case we should note that this is just where the finite collection aperture would contribute an extra term in R^2_{xz} . However, a detailed assessment (appendix) appears to rule out this cause.

The Cr_2O_3 spectra are poorer due to orientation difficulties. However, they are adequate for assignment purposes.

The previous Raman results reported ² for powdered Cr_2O_3 (obtained at this laboratory) appear to be less complete than those reported here. Apart from the difficulties with the Cary 81 spectrometer for such samples (already mentioned), we wish to point out that a 'spike ' filter was not available here for 5145 Å at that time. Thus the 550 cm.⁻¹ region of the spectrum was obscured by a laser background emission.



(a)	P_{xy}	~n zz snt	o cm sensitivity	~ 0
(b)	$I_{\perp} \beta_{xz} \approx -18^{\circ}$	$\sim R^2_{zy}$	8 cm1	imes 5
(c)	$I_{\parallel} \beta_{xz} \approx -18^{\circ}$	$\sim R^2_{zz}$	8 cm1	imes 5
(d)	$I_{\perp} \beta_{zx} \approx -18^{\circ}$	$\sim R^2_{xy}$	8 cm1	imes 5
(e)	$I_{\parallel}\beta_{xy}$	$\sim R^2_{xx}$	8 cm1	$\times 1$
(f)				imes 5
. /				

Low Temperature Studies—A possible criticism of this work lies in the occasional appearance of second-order effects at room temperature and above. It is also important to determine the possible magnetic effects of change of temperature (see later). For these reasons a limited study was made with crystals attached to a liquid nitrogen cold tip *in vacuo* (Figures 3 and 6). The only discernible effects of lowering the temperature were a general sharpening of the bands, and slight frequency shifts. In addition, the slightly ambiguous behaviour of the v_2 band of Cr_2O_3 apparently disappeared at low temperature; the ambiguities are therefore attributed to second-order effects. Frequencies are reported in Tables 5 and 6.

TABLE 5

Raman spectrum of Fe₂O₃ at liquid nitrogen temperature, with excitation at 6328 Å
v 227s, 247w, 294m, 300mw, 415w, 501w, 615w cm.⁻¹

Interpretation.—Despite the close similarity in the masses of chromium and iron, together with the fact that they are in similar positions in the periodic table and have formally d^3 and d^5 ions in these compounds,



FIGURE 4 Further measurements on uncooled α -Fe₂O₃

(a)
$$I_{\parallel}\beta_{zx} \approx -7^{\circ} \sim \mathrm{R}^{2}_{xx}$$
 slit 2.7 cm.⁻¹

The angle of incidence has been allowed to assume a range of values close to the strict Brewster condition to allow for the approximate value of β (6328 Å excitation)

(b)
$$I_{\perp} \beta_{zz} \approx -18^{\circ} \sim R^2_{zy}$$

(c) $I_{\parallel} \beta_{zy} \sim R^2_{yy}$

TABLE 6

Raman spectrum of Cr2O3 cooled by liquid nitrogen, with excitation at 5145 and 4880 Å (see also Figure 6)

ν (cr	n1)
5145 Å	4880 Å
excitation	excitation
291	291
353	352
395	393br
530	526w
552	551
616	616br
	300

FIGURE 5 α -Fe₂O₃ on a liquid nitrogen cold tip *in vacuo* $I_{\parallel} \beta_{zz} = 34^{\circ}$ (a natural face) slit 1.2 cm.⁻¹ (6328 Å excitation)



FIGURE 6 Cr2O3 on a liquid nitrogen cold tip in vacuo (5145 Å excitation)

(a)
$$I_{\parallel} + I_{\perp} \beta_{zz} \approx +18^{\circ} \text{ slit } 2 \text{ cm.}^{-1} \text{ sensitivity } \times 1$$

(b) $I_{\perp} \qquad \beta_{zz} \approx +18^{\circ} \text{ slit } 2 \text{ cm.}^{-1} \text{ sensitivity } \times 2$

there are marked differences between the two spectra. In the case of Fe₂O₃ the spectrum at liquid-nitrogen temperature is essentially the same as that at room

* It is of course difficult to assess the temperature of the crystal at the scattering point due to heating by the laser beam.

temperature. As neutron-scattering results 7 show a clear-cut magnetic phase change between these two temperatures it seems likely that none of the observed bands is due to magnon (or spin-wave) scattering.* For Cr₂O₃ the Neel temperature is only just above room temperature⁸ so that heating by the laser beam (thin crystals glow red-hot) would ensure that the crystal was in the paramagnetic (spin-disordered) state at the scattering point. In view of the weakness and temperature dependance of the frequency of scattering by spinwaves ⁹ we believe that the observed spectra of Fe₂O₃ and Cr₂O₃ are due to phonon scattering. The gross intensity differences between the two spectra are almost certainly due to the presence of absorption bands leading to the possibility of resonance effects.

Factor group analysis¹⁰ of the corundum structure gives $2a_{1g} + 5e_g$ Raman-active fundamentals. In Fe₂O₃ all seven bands are abserved and for Cr₂O₃ six only. We note that e_q bands may appear in xx-yy and xyspectra (where they should be of equal intensity in each case) and in xz-yz spectra. Totally symmetric bands may only appear in xx-yy and zz spectra. These criteria are irrespective of the choice of x and y in the plane perpendicular to z.

A pecularity of Fe₂O₃ is the occurrence of two fundamentals very close to each other. These are of the same (e_q) species, and it is most unusual to find two fundamentals of the same species which apparently overlap. However, the spectral behaviour of both components is unambiguous. At liquid-nitrogen temperatures and under high resolution the bands are almost completely separated (Figure 5).

The problem of the frequency differences between Cr₂O₃ and Fe₂O₃ is more difficult to assess. The spectrum of corundum has been discussed on the basis of discrete Al₂O₃ units,¹⁰ while that of Cr₂O₃ has been discussed in terms of MO₆³⁻ octahedra.² Neither approach is satisfactory. Superficially these structures may be considered as based on a close packing of oxygens with metal atoms in $\frac{2}{3}$ of the octahedral holes. Thus, each metal atom is surrounded by six oxygens in a roughly octahedral array. Similarly each oxygen is surrounded by four aluminiums in a grossly distorted tetrahedral array.

In the case of α -Fe₂O₃ and Cr₂O₃ the vibrations principally involving movement of the oxygen atoms can be discussed from the point of view of this distorted tetrahedron. For a regular tetrahedron M4O involving a heavy metal atom the range 310-469 cm.⁻¹ has been suggested for metal-oxygen vibrations.⁴ It is clear that the magnitude of the distortions in the case of Cr₂O₂ and Fe_2O_3 is sufficient to appreciably widen this range. At present we are carrying out detailed calculations on

7 C. G. Shulh, W. A. Strauser, and E. O. Wollan, Phys. Rev., 1951, 83, 333.

⁸ S. Greenwald, Nature, 1951, 168, 379.
 ⁹ P. A. Fleury, S. P. S. Porto, L. E. Cheeseman, and H. J. Guggenheim, Phys. Rev. Letters, 1966, 17, 84.

S. P. S. Porto and R. S. Krishnan, J. Chem. Phys., 1967, 47, 1009.

these structures and that of corundum itself in an attempt to describe the normal modes of vibration.

EXPERIMENTAL

Crystals of Fe₂O₃ (fluxed) and Cr₂O₃ (flame fusion) were kindly supplied by Dr. Eric White. The ferric oxide exhibited natural faces which made possible morphological setting. In the case of Cr_2O_3 (flame grown) one crystal was set as follows. A random cut face was polished, and some natural cleavage faces were also usable without further treatment. Any face of a crystal shows four orientations, corresponding to two optical extinction directions with $\beta = \pm w^{\circ}$ in each case, for which the difference between I_{\parallel} and I_{\perp} is a maximum. The criterion that (for high symmetry materials) totally symmetric bands must then appear weakly or not at all in I_{\perp} soon enables one to pick out such bands unambiguously. In the case of our crystal of Cr_2O_3 one of the I_{\parallel} spectra showed hardly anything else but the two totally symmetric bands, and it would be an extreme coincidence if this were not because β_{xz} ca. (say) 0 to -30° . Knowing where to look, it was then possible to assign a particular rather poorly developed cleavage as {001}, giving β_{xz} ca. -18°.

Cutting and polishing were done largely by hand with conventional procedures. Final polishing was with 1 micron diamond paste.

All spectra were run on a Spex 1401 monochromator equipped with cooled ITT-FW130 detector and photon counting. Spectra-Physics 125 (He–Ne) and 140 (A^+) lasers were used as sources, with appropriate spike filters.

APPENDIX

The Effect of Finite Aperture of the Collection Lens.— Where the monochromator axis and the electric vector direction of the exciting light coincide with axes used in the description of the Raman tensor, it has been suggested that finite aperture may be allowed for by an equation of the type

$$\mathbf{I}_{i(xy)j} = K(R^2_{yx} + d_j R^2_{jx})$$

where d_j is a 'divergence' factor for the Raman light. For analyser direction k there may be another factor d_k , or in the absence of an analyser $2d = d_j + d_k$. Although originally values of d_j up to 0.3 were found using small crystals on the Cary 81 system, it appears that these were anomalously high due to internal reflections in the crystals. Experiments with liquids generally fail to show this factor unless performed very carefully, and an analysis by Stenhouse ¹¹ may be interpreted in terms of a divergence factor (Table 7) applying to a sample refractive index of unity.

TABLE	: 7
f.no.	2d
1	0.08
2	0.022
3	0.010

The Spex collection lens has an aperture of f/1.6, and it may be seen that the factor is almost negligible. In any case f.no. in the sample (for a *flat* face) ca. $n \times f$.no. in air.

Where the crystal and experimental axes are not lined up, the situation is more complex. In particular, it is no longer true that cross terms $R_{yx}R_{jx}$ are necessarily expected to cancel due to the symmetry of the transmission function for the lens about its axis, particularly where the crystal face is at an angle to the lens. A simple six-strip numerical integration was therefore carried out for I_{\parallel} , ignoring the d factor arising as in (3), *i.e.* for the aperture of the lens in a direction away from the plane defining I_{\parallel} , and with the following assumptions: (i) Integration with respect to dr', where r' is the angle within the sample, between the Raman ray considered and the normal to the surface. (ii) Transmission across the sample surface according to the simple Fresnel formula $I/I_0 = 1 - [\tan^2 (i' - r')]/[\tan^2 (i' + r')]$ or $1 - [(n-1)/(n+1)]^2$ at perpendicular incidence. (iii) Lens transmission function proportional to the angle subtended in air at the sample face by the appropriate infinitesimal strip $d\delta$.

Although this procedure involves various assumptions, e.g. in (iii) that $\sin (\alpha/2) = \alpha/2$ where α is the angular aperture, (so that i' = nr') the results should show what sort of correction factors might apply. As may be expected the largest term apart from C_{zz}^3 in measurements made according to Figure 1 with $\beta_{zz} = -6^\circ$ is in $R_{zz}R_{zz}$. Even so, this is insufficient to account for a discrepancy in the $\beta_{zx} = -6^\circ$ spectrum observed for Fe₂O₃. The results are included in Tables 1 and 2. The relative perfection of measurements made according to Figure 1 with $\theta = 90^\circ$ is another reason for ideally preferring that method. A Fortran computer programme was written for the evaluation of the results in Tables 1 and 2, and a copy may be obtained on application to Dr. Gilson. (Specify lineprinter listing or ICT 1900 card.)

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¹¹ I. A. Stenhouse, Ph.D. Thesis, Cambridge University, 1968.