

MINERALOGICAL MAGAZINE

VOLUME 38 NUMBER 295 SEPTEMBER 1971

Yttrotungstite

R. J. DAVIS

Mineralogy Department, British Museum (Natural History), Cromwell Road, London, S.W. 7

AND G. W. SMITH

British Petroleum Co. Ltd., B.P. Research Centre, Sunbury-on-Thames, Middlesex

SUMMARY. Yttrotungstite occurs at Kramat Pulai mine, and at Tapah, Kinta, Perak, Malaysia, as yellow earthy material and as monoclinic laths, elongated along [001], flattened, and always twinned, on {100} to pseudo-orthorhombic symmetry, and frequently bevelled by {110}; crystals are very rarely terminated by {101}. $\gamma = [010]$, $\alpha: [001] = 26^\circ$, probably in β acute, and $2V_\alpha \simeq 68^\circ$. A thermal weight loss curve and an infra-red absorption spectrum are given and discussed. Accessory minerals include raspite and stolzite.

The yttrotungstite unit cell has a 6.95, b 8.64, c 5.77, β $104^\circ 56'$, space group $P2_1/m$; cell contents are $(\text{Yt, Ln, Ca, Mg})_2(\text{W, Al, Si, Ti, Fe})_4(\text{O, OH})_{14}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. Indexed X-ray powder data are given. Microprobe studies show that Al and Si replace W and are concentrated in zones showing larger values of $a \sin \beta$ (6.75 Å instead of 6.72 Å) but with no other appreciable difference in cell dimensions. Crystal structure studies show that the structure consists of WO_6 octahedra sharing non-opposite edges in zig-zag chains running parallel to [010]. Yttrium is in approximately trigonal prismatic coordination between the chains, with the water molecule as a seventh neighbour at one prism face. The water molecule is accommodated in the angle between zig-zags in the WO_6 chains; it is probably hydrogen bonded to chain oxygen atoms, and becomes coordinated to the yttrium by a shear between chains away from strict close-packing of the oxygen atoms. The shear is related to the change in $a \sin \beta$ in (Al, Si)-rich zones; arguments based on this and on details of the chemical analysis suggest that SiO_4 replaces WO_6 with a local oxygen deficit.

Oxygen atom peaks on partial Fourier difference syntheses for our data for yttrotungstite are only slightly larger than the troughs in the syntheses due to experimental error. Methods of testing the significance of the positive peaks are described in an appendix.

SCRIVENOR and Shenton (1927) described thorotungstite, occurring as shapeless blocks at the base of a tin-bearing alluvial deposit overlying tourmaline granite at the Kramat Pulai mine, Pulai, Kinta district, Perak, Malaysia. The name was given on the basis of a chemical analysis showing ThO_2 and WO_3 as the main constituents; Beard (1950)¹ referred to a new unpublished analysis of material from the type locality showing that what was taken to be ThO_2 by Shenton in fact consists of rare earths, dominantly yttria. Beard proposed the revised name *yttrotungstite* for this mineral, a name that is now accepted.

¹ Butler (1957) gives the author of this reference as E. H. Bradshaw, while Semenov *et al.* (1965) attribute it to R. Bradshaw. In fact it was published over the initials E. H. B. and was written by Dr. E. H. Beard, the editor of the journal. The analysis has subsequently been published by Bradford (1961).

Butler (1957) analysed the rare earths in a specimen of yttritungstite from the type locality, from Dr. Bradshaw of the Malay Geological Survey. He found that while yttria dominated the analysis and lanthanons of even atomic number predominated over those of odd atomic number, the concentration variations within each class were relatively small. Semenov, Kataeva, and Rudnitskaya (1965) examined Butler's sample¹ and gave a full chemical analysis, additional rare earth analyses, X-ray powder data, optical properties, D.T.A. and weight-loss heating curves, and an infra-red absorption spectrum. They suggested the formulae² $\text{Yt}_2\text{W}_5\text{O}_{14}(\text{OH})_8$ or $\text{YtW}_3\text{O}_9(\text{OH})_3$.

The authors independently undertook X-ray studies of yttritungstite. Our results when compared were in satisfactory agreement and we were able jointly to derive the crystal structure of yttritungstite and a more satisfactory formula. We are grateful to many colleagues for further details of its physical properties.

Specimens. We have studied all specimens of yttritungstite in the British Museum (Natural History) collection, namely B.M.1921,395, B.M.1927,1157-60, B.M.1948, 435, and B.M.1969,165-70, all from the type locality. We have also studied GR.740, collected by Dr. G. V. Wood from a mine dump at Tapah, Kinta district, Perak, Malaysia. A portion of this sample has been presented to the British Museum (Natural History) collection as B.M.1969,227.

All the specimens studied consisted mainly of a fine-grained aggregate of pale-yellow earthy yttritungstite, with rare druses lined by yttritungstite crystals. The yttritungstite was sometimes admixed with large rounded quartz grains. Both earthy and crystalline yttritungstite gave the same characteristic X-ray powder pattern as was given³ by the samples of analysed material referred to by Beard (1950).

In a survey of accessory minerals, J. G. Francis and Miss E. E. Fejer have identified by X-ray powder photographs: frequent patches of white earthy kaolinite, also quartz, muscovite, hydrobiotite, illite, haematite, and a new mineral, which has proved to be the aluminium analogue of ferritungstite. Rare, probably allogenetic, crystals of tourmaline, scheelite, rutile, and cassiterite were identified; cassiterite also occurred as yellow earthy varlamoffite. Fine grained stolzite and raspite were identified, raspite being also present as crystals in the druses. The associated minerals agree well with the description given by Bradford (1961) of the paragenesis of tin and tungsten ores especially at Kramat Pulai.

Crystals from GR.740 and B.M.1927,1157 were selected for detailed study. Several grams of earthy yttritungstite from B.M.1927,1157 were crushed through 300 mesh; this material will be referred to below as Sample E. X-ray powder photographs (11.46 cm diameter camera) showed that Sample E was essentially pure yttritungstite, but on diffractometer traces and focusing-camera photographs it was possible to observe a few extremely weak extra lines. Some of these could be attributed to a few per cent of the aluminium analogue of ferritungstite, and a weak sharp line at 7.2 \AA

¹ Semenov *et al.* (1965) state that their sample was No. 3306 from the British Museum. No specimen of yttritungstite answers this description in the British Museum (Natural History) collection and Dr. Butler confirms that their specimen was a portion of the material he studied.

² At the editor's suggestion we use here the old symbol, Yt, for yttrium to avoid confusion with Y used as an algebraic symbol or to indicate an atomic site.

³ Films X4658, X4660, ref. M 5419/37, British Museum (Natural History).

was attributed to a trace of kaolinite. Mr. R. F. Symes has isolated a minute fraction of sample E that floated at 3.2 gm/cm³. This consists dominantly of white grains of a fine-grained intergrowth (smooth powder lines) of yttrotungstite with muscovite or more probably illite. Traces of quartz, calcic plagioclase, and gypsum were also identified in the floating fraction.

X-ray data. Oscillation, rotation, and equi-inclination Weissenberg photographs show that the crystals of yttrotungstite are monoclinic, space group $P2_1$ or $P2_1/m$. We derive below a satisfactory structure for yttrotungstite in $P2_1/m$. All the crystals were laths, flattened on {100} and elongated along [001], and poorly oriented, showing a mosaic spread of at least 4°. All the crystals studied (about 40) were twinned on {100}; this accounts for the orthorhombic symmetry reported by Scrivenor and Shenton. Characteristic effects on all Weissenberg photographs around [001] and [010] except

TABLE I. *Yttrotungstite cell dimension measurements. Figures given in brackets are estimated errors in the last unbracketed digit (in col. 1 the error is the 95 % confidence limit = 2.15σ)*

	1	2	3	4	5	6
<i>a</i>	6.954(6) Å	—	—	—	—	—
<i>b</i>	8.637(9) Å	8.632(2)	8.633(3)	8.631(2)	8.635(3)	8.627(2)
<i>c</i>	5.771(6) Å	—	—	—	—	—
β	104° 56'(4)	—	105° 7'(4)	105° 4'(5)	105° 4'(7)	105° 0'(4)
<i>a</i> sin β	6.718(7) Å	6.714(3)	6.718(3)	{ 6.715(3) 6.750(6)	6.718(2) 6.748(5)	6.715(4) 6.746(8)
<i>c</i> sin β	5.576(6) Å	—	5.572(4)	5.575(2)	5.580(4)	5.578(4)
V	334.8(7) Å ³	—	—	—	—	—

1. Mean of two determinations on Sample E, agreeing to 0.02 %, in a Nonius de Wolff focusing camera using Cu-K α radiation and the lines detailed in table II. Calibrated samples of SnO₂ and NH₄Cl respectively were used as internal standards. Measurements were refined by Hess's (1951) least-squares method, assuming unknown film shrinkage errors and camera errors in 2θ proportional to $\tan 2\theta$.

2 to 6. Results by Farquhar and Lipson's (1946) method from pairs of symmetrical back reflection oscillation photographs taken around *c* and *b* for crystals from B.M.1927,1157. β was derived from the *b*-axis oscillation photograph taken along *c*, and is thus an average value for the two lattices in the peristerite effect, whose separate reflections were not resolved on this photograph.

for (*hko*) showed that the twinning was on a gross scale, with opposite faces of the laths belonging predominantly to opposite twins.

Cell dimension data for yttrotungstite are given in table I. Data from Sample E (col. 1) and for the first two crystals (cols. 2 and 3) are in excellent agreement. However, many yttrotungstite crystals showed a peristerite¹ effect in which high-angle reflections near *a** were resolved into two α_1/α_2 doublets indicating two lattices in parallel orientation with the same *b* and *c* dimensions but differing slightly in *a* sin β .

¹ Name given by analogy with the crystallographically similar effect of this name observed in feldspars.

From table I, the lattice common to all crystals has the same dimensions as the earthy material, and the second, larger lattice occurs only in certain crystals.¹

Powder data, indexed with the help of single crystal intensities, are given in table II and are more complete than those of Semenov *et al.*, who used a smaller camera.

TABLE II. X-ray powder data for ytrotungstite; yellow-brown laths from B.M.1927, 1157, Kramat Pulai mine, Kinta, Perak, Malaysia; film 748Fa taken in an 11.46 cm diameter camera with filtered Cu-K α radiation

d_{obs}	I	d_{calc}	hkl	d_{obs}	I	d_{calc}	hkl	d_{obs}	I	d_{obs}	I
6.73 Å	ms	6.716 Å	100*	2.554 Å	mw	2.557 Å	031*	1.990 Å	mwB	1.284 Å	m
5.57	mw	5.576	001*	—	—	2.491	131†	1.914	w	1.260	mw
—	—	5.301	110†	2.486	m	2.486	202‡	1.872	w	1.246	w
4.98	s	4.972	101*	—	—	2.484	211†	1.828	mw	1.226	vwv
4.69	vvs(2)	4.684	011*	—	—	2.389	212†	1.796	mw	1.205	mw
4.32	mw	4.317	020§	—	—	2.379	122†	1.760	mw	1.188	w
—	—	4.309	111†	2.375	vwv	2.366	102	1.737	mw	1.169	vw
3.83	m	3.829	101*	—	—	2.342	022†	1.707	w	1.152	vwB
3.63	m	3.631	120*	—	—	2.300	131	1.678	vwv	1.136	vw
3.51	vw	3.500	111*	2.302	w	2.294	301	1.652	ms	1.110	mw
—	—	3.413	021†	—	—	2.282	112†	1.609	vwv	1.094	w
3.36	ms	3.358	200*	2.239	m	2.239	300*	1.594	m	1.085	mw
3.26	vvs(1)	{ 3.278 3.260	{ 201 121	—	—	{ 2.223 2.217	{ 221 311†	{ 1.571 1.534	{ wB	{ 1.064 1.054	{ vw w
3.13	w	3.130	210*	—	—	2.185	230†	1.538	mw	1.039	mw
3.07	m	3.064	211*	—	—	2.167	310†	1.505	w	1.027	vwv
2.869	ms	2.864	121	—	—	2.163	231†	1.473	mwB	1.013	vwv
—	—	2.851	102†	2.159	w	2.158	040	1.455	w	0.984	vwv
2.790	ms	2.788	002*	—	—	2.154	222†	1.438	mw	0.975	vw
—	—	2.707	112†	2.079	w	2.075	122*	1.421	w	0.957	mwB
—	—	2.653	012†	—	—	2.055	140†	1.395	vw	0.938	mwB
2.650	ms	{ 2.650 2.645	{ 220 130‡	2.028	vs(3)	{ 2.026 2.025	{ 321 132	{ 1.381 1.350	{ vwv	{ 0.907	{ mwB
—	—	2.611	221†	—	—	2.021	302	1.322	vwB	—	—
2.597	mw	2.594	201‡	—	—	2.013	041†	1.296	vw	—	—

* Lines used for cell dimension determination (see table I, col. 1) and for intensity measurements (see below).

† Reflections weak or absent on single crystal photographs.

‡ Lines used for cell dimensions only.

§ Line used for intensities only.

|| The 221 reflection appeared extremely weakly on focusing camera photographs and was used for cell dimension determination.

Diffractometer traces of Sample E showed evidence of preferred orientation in which the c axis, and to a slightly lesser extent the b axis, tended to lie in the plane of the specimen surface, even when the powder was dispersed in plastic, suggesting that the fine-grained material is morphologically similar to the crystals.

¹ The difference in $a \sin \beta$ between the two lattices is such that if the second lattice were present in Sample E it would give rise to easily resolvable doublets on focusing camera photographs.

Microprobe studies were made by Dr. S. J. B. Reed and Mr. R. F. Symes on crystals from B.M.1927,1157, using a Cambridge Geoscan. Twenty-one crystals were sorted, using X-ray back reflection oscillation photographs with the beam nearly perpendicular to (100), into three classes: four *one-lattice* crystals showing no evidence of the second yttritungstite lattice: ten *intermediate* crystals showing the second lattice weakly: and seven *peristeritic* crystals showing the second lattice as strongly as the first. The crystals were mounted on Durofix and examined in the Geoscan without polishing.

Forty-one measurements of the ratio of X-ray intensities from tungsten and yttrium respectively (L_{α_1} lines at 25 kV, corrected for background) gave means and standard deviations showing no significant difference between the three classes. The peristerite phenomenon is therefore probably unconnected with major constituents such as these elements or the lanthanons.

Twenty-four measurements of the contents of Al and Si, using K_{α} X-ray lines at 20 kV, were expressed uncorrected as wt % oxides relative to a topaz standard; corrected results might be higher by a factor of up to 1.5. About half the results showed <0.05 wt % Al_2O_3 , with SiO_2 in the range 0.3–0.7 wt %; the remainder showed comparable amounts of Al_2O_3 and SiO_2 ranging up to 7.3 wt % Al_2O_3 and 11.1 wt % SiO_2 in peristeritic crystal 3. Scanning photographs of this crystal in fig. 1

show high local concentrations of Al and Si coinciding on the crystal surface. Further scanning photographs of four crystals from each class showed perfect correlation with the peristerite effect: one-lattice crystals showed virtually no Al, Si concentrations; intermediate crystals showed small concentrations; peristeritic crystals showed extensive Al, Si concentrations. Al and Si concentrations always coincided. Ca and Mg showed no concentrations within the crystals. A typical line scan across an Al, Si concentration is shown in fig. 2a, taken from the crystal of fig. 1. The traces for Al and Si rise simultaneously to about the same extent, indicating *ca.* 10 wt % of each oxide, and wherever this happens the traces for both W and Yt fall.

The peristerite phenomenon is thus associated with high surface concentrations of Al and Si, but the amounts found are far too large to be accommodated in the yttritungstite lattice and thus apparently indicate a second phase. Moreover, despite the Yt trace in fig. 2a, it is crystallochemically impossible for Al and Si to replace an atom as large as Yt. However, with concentrations as large as those shown in fig. 1, if the second phase extends to any depth it should give evidence on the X-ray single crystal photographs; such evidence was not observed. These high concentrations of Al and Si thus represent a thin surface layer only. A rough calculation shows that an aluminosilicate layer about $0.1 \mu m$ thick would give apparent oxide concentrations of several per cent, and would reduce the intensity of the Yt- L_{α_1} line from the underlying yttrium by about 10 %, relative to the W- L_{α_1} line intensity. This model thus

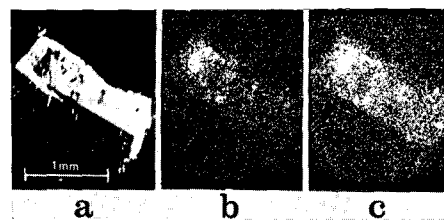


FIG. 1. Scanning photographs of peristerite-type crystal 3 from B.M.1927,1157. (a) Secondary electrons from the crystal. The scale mark should read 0.1 mm. (b) Al- K_{α} radiation. (c) Si- K_{α} radiation.

explains the constancy of the W:Yt ratio found above, without postulating the replacement of Yt by Al and Si.

Five yttritungstite crystals (not examined by X-rays) were polished to show their internal cross-section. Scanning photographs showed coincident Al,Si concentrations on some of the crystals, entirely confined to the crystal edges. Twenty-four measurements on two crystals away from the Al,Si concentrations, showed a uniform content

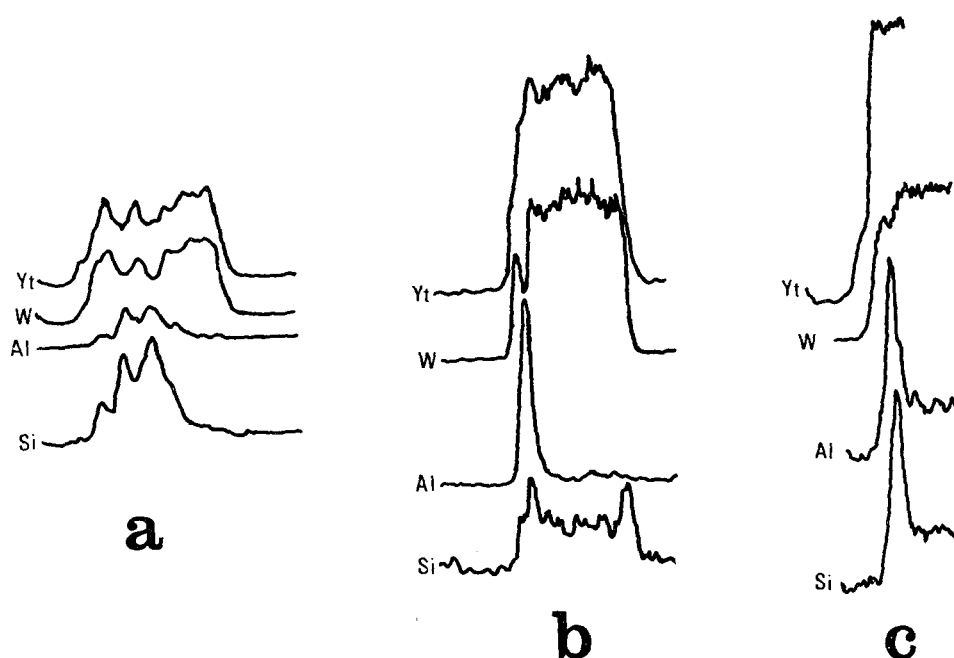


FIG. 2. Line scans across three crystals of yttritungstite from B.M.1927,1157, made with Yt- $L\alpha_1$, W- $L\alpha_1$, Al- $K\alpha$, and Si- $K\alpha$ radiations respectively. The horizontal scales in each of (a) to (c) are arbitrary and different arbitrary vertical scales are used for each of the twelve traces. (a) scan across surface of crystal 3 illustrated in fig. 1. (b) scan across edge of a polished section through crystal 4/3. (c) similar scan across the edge of crystal 4/2.

of 0.2 wt % SiO_2 (uncorrected), qualitatively confirming the surface measurements. A number of line scans across Al,Si concentrations showed the same features, but none was ideal owing to the proximity to the edge of the crystal and possible edge effects. The scan of fig. 2b shows clearly that where the Al trace rises sharply the W trace dips while the Yt trace is unaffected. The Si trace rises unusually little on this scan, and is more typical in fig. 2c, which shows the same effects otherwise as fig. 2b, but less convincingly distinguished from edge-effects.

Figs. 2b and 2c show that beneath the thin aluminosilicate surface layer postulated above are yttritungstite zones enriched in Al and Si replacing W. These zones explain the presence of the second yttritungstite lattice and occur only in the surface layers of the crystals; since the crystals are highly absorbing to X-rays, only their surface

layers diffract, and X-ray single crystal photographs exaggerate the overall content of (Al,Si)-rich zones. The sharpness of the X-ray reflections from the second yttrotungstite lattice shows that the zones are of very uniform composition, suggesting that this is defined by solid solubility limits, probably of Si in yttrotungstite.

This work provides proof, for the first time, that Si (as well as Al) can replace W in tungstate minerals.

From the results obtained above from X-ray focusing camera photographs of Sample E, the (Al,Si)-rich zones are absent from the earthy material and must have become incorporated into the large yttrotungstite crystals as they recrystallized around the druses in the earthy matrix. The temperature of this process is limited by the observation of crystals of raspite in the druses; raspite inverts rapidly to stolzite¹ at 410 °C.

The Al and Si are probably derived from clay minerals. These may have been imported with the ground water from the alluvial layer overlying the yttrotungstite *in situ*. Alternatively the clay is the illite (or muscovite) observed in Sample E. The thin surface film of aluminosilicate may be a residue of unadsorbed clay or alternatively be attributed to etching by relatively acid ground-water. Any complete explanation of the (Al,Si)-rich zones must also explain why they are confined to the surface layers of the yttrotungstite crystals.

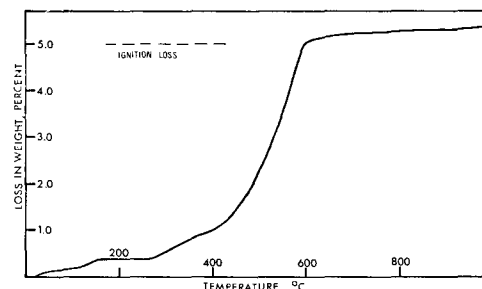


FIG. 3. Weight-loss curve obtained on 163 mg of sample E in a Stanton Thermobalance. The ignition loss, obtained by Dr. A. A. Moss in a partial analysis of this sample, is shown for comparison

Heating experiments. Fig. 3 shows a weight-loss heating curve obtained by Mr. C. J. Elliott, which agrees well with that of Semenov *et al.* The weight-loss occurs in two stages: about 0.4 % is lost at temperatures up to 150 °C, and the remaining 4.8 % is lost between 250° and 600 °C, mainly above 400 °C. This behaviour is very similar to that of the clay impurities found in Sample E, which lose adsorbed water at 150 °C but retain structural water up to 500 °C.

The infra-red spectrum of fig. 4 was obtained by Mr. C. J. Elliott. A similar spectrum was obtained from crystals of GR.740. The spectra are in good agreement with that given by Semenov *et al.* but are extended to lower and higher wavelengths. Semenov *et al.* attribute the strong absorptions in the range 9 to 14 μm to W-O vibrations, since they are similar to those found in the spectra of tungsten hetero-poly acids. However, their assignment of the small peak at 1440 cm^{-1} ($6.94\ \mu\text{m}$) to OH stretching vibrations appears to be a mistake, since these usually absorb in the range $2.85\text{--}2.90\ \mu\text{m}$ (here $2.87\ \mu\text{m}$) while the peak at $6.1\ \mu\text{m}$ in fig. 4 is attributable to H-O-H bending vibrations. This last peak shows that at least some of the hydrogen in yttrotungstite is in the form of discrete water molecules. The identity of these peaks was verified

¹ G. F. Claringbull and D. McKie, unpublished work, X 6363.

on a portion of sample E heated 7 hours at 130 °C, when the spectrum was unchanged, and on the sample used for the thermobalance experiment to 750 °C when these peaks were eliminated and the spectrum completely changed. Mr. Elliott also noted the small peak at 3.35 μm , which resembles that attributed to 'co-ordinated water' in the infra-red spectrum of $\text{LiOH}\cdot\text{H}_2\text{O}$ by Jones (1954), and the presence of this peak was verified at a higher sample concentration.

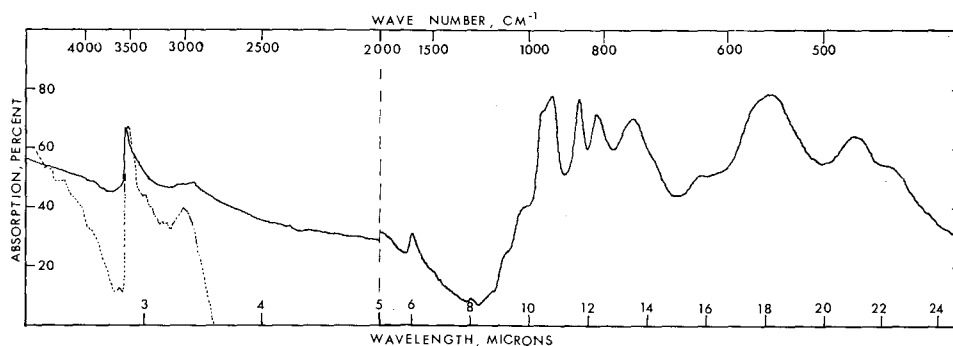


FIG. 4. Infra-red absorption spectrum No. 1332 obtained for Sample E using a Grubb Parsons Spectromaster. For the solid curve the sample was at 0.5 wt % concentration in a KBr disc; for the dotted curve the sample was at 3 wt % concentration.

Morphology. Crystals from our specimens were too small to measure goniometrically. Like the crystals figured by Scrivenor and Shenton (their fig. 1), many of our lath-like crystals were sharply bevelled on their long edges. Seven measurements in silhouette on two mounted crystals gave the angle $36.9 \pm 3^\circ$, which identifies the beveling face as (110) [(110):(100) = 37.9°]. Terminal faces as shown in Scrivenor and Shenton's fig. 1 were extremely rare on our material and we have found only one crystal from B.M.1921,395 showing such a face. Two independent settings gave angles of 57° and 60° in silhouette. An X-ray oscillation photograph was too poor to identify whether the face-normal lay in β acute or β obtuse, but the only simple face fitting these measurements is (10 $\bar{1}$) [(10 $\bar{1}$):(100) = 59.4°].

Cleavage. We have verified the presence of the two cleavages given by Scrivenor and Shenton. That running along the laths is (010); that running across the laths is less well defined, due to the twinning, but structural results below suggest that it probably lies on (10 $\bar{1}$).

Specific gravity. Dr. R. Walls found D 5.96 on crystals from GR.740 (Berman balance) and we accept this as the most reliable value. Earlier results (5.85, Semenov *et al.*; 5.55, Scrivenor and Shenton) are presumably on impure earthy material. Mr. A. J. Easton found D 5.55 pyknometrically on Sample E; if this contained, say, 5.8 % kaolinite, the corrected specific gravity would become 5.96.

Optical properties. Semenov *et al.* obtained α 1.89 pale yellow, β 1.98, γ 2.02 dark yellow, on earthy material. Mr. P. G. Embrey found that crystals from GR.740 were length fast, had a birefringence about 0.12 and probably gave a β -axis interference

