

SUBDIVISION OF THE PYRITE GROUP, AND A CHEMICAL AND X-RAY-DIFFRACTION INVESTIGATION OF ULLMANNITE

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ABSTRACT

Minerals in the pyrite group, with the chemical formulae of $4MXY$ and a pyrite-type crystal structure, are divided into three categories: pyrite (cubic space-group $Pa\bar{3}$), ullmannite (cubic space-group $P2_13$) and cobaltite (orthorhombic space-group $Pca2_1$). Wilyamite $CoSbS$ belongs to the cobaltite subgroup. The species names of gersdorffite- $Pa\bar{3}$, gersdorffite- $P2_13$, and gersdorffite- $Pca2_1$ have been approved by IMA. Ullmannite, with the end-member composition $NiSbS$, is isotropic and probably belongs to cubic space-group $P2_13$. Electron-microprobe analyses of nine ullmannite specimens show substitution solid-solution of Sb by up to 10.3% As and 4.6% Bi, and of Ni by up to 3.3% Co and 0.2% Fe, but almost no substitution solid-solution for S. The strength of the optical anisotropism in ullmannite is correlated with the molecular percentage of $(Co,Fe)AsS$ as well as the intensity of the reflections forbidden by cubic space-group $P2_13$ ($h00$ with h odd). Partial ordering of As within the four Sb sites and four S sites in ullmannite has been previously determined. These observations may be explained by a sextuplet of interpenetrating, twin-related, orthorhombic (space group $Pca2_1$) domains of $(Co,Fe)AsS$ about a $\bar{3}$ twin axis [111] within the cubic (space group $P2_13$) structure of ullmannite.

Keywords: pyrite group, ullmannite, wilyamite, gersdorffite, order-disorder, microprobe analyses, optical anisotropism, X-ray diffraction, twinning.

SOMMAIRE

Les minéraux du groupe de la pyrite, de formule chimique du type $4MXY$ et de structure cristalline du type pyrite, se subdivisent en trois types structuraux: pyrite (cubique $Pa\bar{3}$), ullmannite (cubique $P2_13$) et cobaltine (orthorhombique $Pca2_1$). La wilyamite $CoSbS$ appartient au sous-groupe de la cobaltine. Les noms d'espèces gersdorffite- $Pa\bar{3}$, gersdorffite- $P2_13$, et gersdorffite- $Pca2_1$, ont été approuvés par l'IMA. L'ullmannite, dont la composition est celle du pôle $NiSbS$, est isotrope et fait probablement partie du groupe spatial $P2_13$. L'analyse de neuf spécimens d'ullmannite à la microsonde électronique a établi la solution solide de substitution de Sb par As (jusqu'à 10.3% As) et Bi (4.6%), ainsi que celle de Ni par Co (3.3%) et Fe (0.2%); la même analyse, par contre, n'a trouvé presque pas de substitution de S. L'anisotropie optique de l'ullmannite est en corrélation avec le pourcentage moléculaire de $(Co,Fe)AsS$ comme l'est aussi l'intensité des réflexions interdites par le groupe $P2_13$ ($h00$ à h impair). L'ordonnance partielle de As parmi les quatre sites de Sb et les qua-

tre de S de l'ullmannite a été déterminée précédemment. Ces observations peuvent s'expliquer par une macle sextuple de cristaux orthorhombiques- $Pca2_1$ qui s'interpénètrent autour d'un axe ternaire de macle $\bar{3}$ suivant [111] en notation cubique.

(Traduit par la Rédaction)

Mots-clés: groupe de la pyrite, ullmannite, wilyamite, gersdorffite, relation ordre-désordre, analyses à la microsonde, anisotropie optique, diffraction X, macle.

INTRODUCTION

Ullmannite (Ramsdell 1925, Peacock & Henry 1948, Bokii & Tsinobev 1954, Takéuchi 1957, Pratt & Bayliss 1980) has a pyrite-type crystal structure. In the chemical formula of ullmannite $4NiSbS$, the Sb is ordered in one set of four sites, whereas the S is ordered in the other set of four sites. A crystal-structure refinement of arsenian ullmannite by Bayliss (1977) showed that As is probably concentrated in one of the four Sb sites and in one of the four S sites. Such ordering would reduce the symmetry from cubic space-group $P2_13$, allow reflections forbidden by cubic space-group $P2_13$, and explain why arsenian ullmannite is anisotropic.

King & Prewitt (1979) suggested that the results of Finklea *et al.* (1976) and Bayliss (1977) on pyrite disagree. Finklea *et al.* (1976) have refined the crystal structure of a pyrite specimen in cubic space-group $Pa\bar{3}$. Their specimen was obtained from the Commercial Ore kyanite mine from the metamorphic belt in South Carolina. Since kyanite is the product of medium-grade regional metamorphism (Berry & Mason 1959), their pyrite specimen was formed at moderately high temperature and pressure. Evans *et al.* (1982) showed by Mössbauer spectroscopy that there are two distinct types of pyrite. Pauling (1978) suggested a chemical reason for the two crystal structures of pyrite based upon the presence or absence of resonance between two types of S bonding. Since the pyrite of Finklea *et al.* (1976), formed at a high temperature, is expected to be cubic, and the pyrite of Bayliss (1977), formed at low temperature, is expected to have a lower symmetry, there is no disagreement between the results of Finklea *et al.* (1976) and Bayliss (1977).

If the intensity of a Bragg reflection should

become unobservable at any angle as the crystal is rotated about a scattering vector, then the observed intensity is attributed to multiple diffraction. Therefore, it is relatively easy to prove multiple diffraction by finding a single angular position with an unobservable intensity. On the other hand, King & Prewitt (1979) showed that many multiple reflections occur from a CuS_2 sample with a pyrite structure, and concluded that it is extremely difficult with four-circle goniometry to prove that the extra reflections are not caused by multiple diffraction.

Optical anisotropy may be either intrinsic to the crystal structure or a surface feature. Besides the microscope considerations of perfectly crossed nicols, exact centring of light, and aberration-free optics, the polished block should be free from surface features such as relief, scratches, strains and etching. The members of the pyrite group that display orthorhombic symmetry and space group $Pca2_1$, such as cobaltite and cobaltian gersdorffite (Bayliss 1982a, b), are optically anisotropic owing to crystal structure. King & Prewitt (1979) found that CuS_2 , which is a cubic member of the pyrite group (space group $Pa3$), is optically anisotropic. On the other hand, all seven specimens of sperrylite, which is a cubic member of the pyrite group (space-group $Pa3$), were found to be optically isotropic by Klemm (1962). Therefore, it is possible to prepare a polished block of a mineral in the pyrite group without surface features (relief, scratches, strains and etching). Optical observations by Klemm (1962) indicate that seven out of eight specimens of ullmannite contain anisotropic areas in a polished block, and suggest that the optical anisotropy of ullmannite is caused by chemical variations.

Since the existing evidence for deviations from cubic symmetry by ullmannite is not substantial, further specimens of ullmannite were investigated. Since many new minerals with a $4MXY$ chemical formula and a pyrite-type crystal structure have been described, and a clear distinction between the ullman-

nite and cobaltite subgroups is now possible, a classification of these minerals is now appropriate.

SUBDIVISION OF THE PYRITE $4MXY$ GROUP

Mineral species with a $4MXY$ chemical formula and a pyrite-type crystal structure have four metal atoms ($4M$) that occupy similar atomic positions in all three subgroups (Tossell *et al.* 1981). These subgroups are based upon the disorder or different ordering-schemes of the eight nonmetal atoms ($4X + 4Y$) in eight atomic positions. The cobaltite group of Fleischer (1983), which contains mineral species with different ordering-schemes, should be subdivided.

The pyrite subgroup in the cubic space-group $Pa3$ has eight nonmetal atoms ($4X + 4Y$) equally distributed (disordered) over the eight atomic positions on the threefold axes (Fig. 1). The disorder and high symmetry are shown by the absence of the 010 and 011 reflections.

The ullmannite subgroup in the cubic space-group $P2_13$ has eight nonmetal atoms ($4X + 4Y$), where the $4X$ atoms are ordered in one set of four atomic positions on the threefold axes and the $4Y$ atoms are ordered in the other set of four atomic positions on the threefold axes (Fig. 1). The order and reduction in symmetry from cubic space-group $Pa3$ to cubic space-group $P2_13$ allow each set of four atoms to move along the threefold axes. The lower symmetry of cubic space-group $P2_13$ is shown by the absence of the 010 reflection and the presence of the 011 reflection.

The cobaltite subgroup in the orthorhombic space-group $Pca2_1$ is pseudocubic. The eight nonmetal atoms ($4X + 4Y$) are ordered, with $4X$ atoms in one set of four atomic positions and $4Y$ atoms in the other set of four atomic positions (Fig. 1). Figure 1 shows the crystal structure as it appears projected along the three pseudocubic axes. The order and reduction in

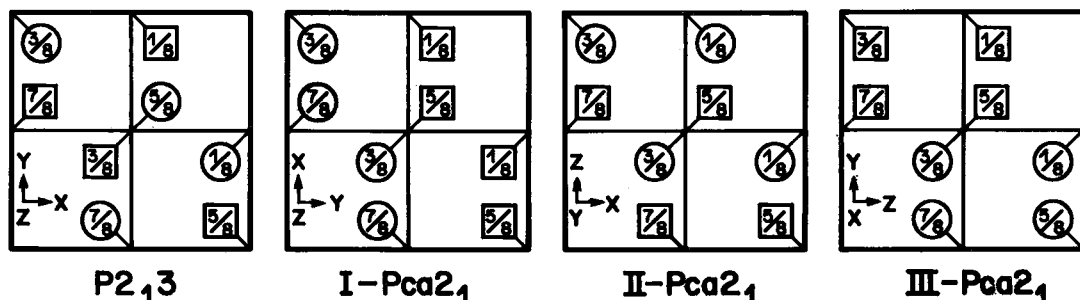


FIG. 1. Atomic positions in pyrite-group minerals. The circles and squares are used to denote the elements X and Y , respectively, in the general formula $4MXY$. A line connects every nonmetal pair X and Y . $I-Pca2_1$, $II-Pca2_1$ and $III-Pca2_1$ represent different orientations of the pseudocubic structure related by a $\bar{3}$ twin axis $[111]$.

TABLE 1. CRYSTAL-STRUCTURE CLASSIFICATION OF THE PYRITE MX₂ GROUP

Pyrite subgroup <i>Pa3</i>		Ullmannite subgroup <i>P2₁3</i>		Cobaltite subgroup <i>Pca2₁</i>	
NiAs	Gersdorffite- <i>Pa3</i>	NiAs	Gersdorffite- <i>P2₁3</i>	(Ni,Co)As	Gersdorffite- <i>Pca2₁</i>
RhAs	Hollingworthite	NiSbS	Ullmannite	CoAs	Cobaltite
IrAs	Irarsite	IrSbS	Tolovkite	CoSbS	Willyamite
PtAs	Platarsite	PdSbTe	Testibiopalladite		
PtBiSb	Insizwaite	PdBiTe	Michenerite		
		PtBiTe	Maslovite		

symmetry from cubic space-group *Pa3* to orthorhombic space-group *Pca2₁* allow each set of four atoms to move off the threefold axes. The lower symmetry of orthorhombic space-group *Pca2₁* is shown by the presence of the 010 and 011 reflections (Entner & Parthé 1973).

The powder X-ray-diffraction data of willyamite CoSbS in PDF 26-1106 include the 010 and 011 reflections. The *hk0* and *Ok1* precession photographs of a willyamite crystal and the pseudocubic unit-cell parameter determined with a single-crystal diffractometer by Cabri *et al.* (1970) are similar to those of cobaltite (Bayliss 1982a) and cobaltian gersdorffite (Bayliss 1982b). Therefore, willyamite is pseudocubic, and probably has a sextuplet of orthorhombic space-group *Pca2₁* interpenetrating twin-related domains (Fig. 1) about a $\bar{3}$ twin axis [111].

Minerals in the pyrite group may be divided into pyrite, ullmannite and cobaltite subgroups based upon the 010 and 011 reflections in powder X-ray-diffraction data. The subgroups, which are listed in Table 1, are based upon the powder X-ray-diffraction data in the Group Data Book of the Mineral Powder Diffraction File by Bayliss *et al.* (1983).

The group name gersdorffite should be used where the ordering scheme of the nonmetal atoms is unknown. The names of the mineral species gersdorffite-*Pa3*, gersdorffite-*P2₁3* and gersdorffite-*Pca2₁* should be used where the ordering scheme of nonmetal atoms is known. This nomenclature system has been approved by the International Mineralogical Association, Commission on New Minerals and Mineral Names.

METHODS AND RESULTS

Nine specimens of ullmannite were obtained for this investigation from the British Museum (BM), Australian Museum (AM) and the Royal Ontario Museum (ROM). The specimens, which have previously been studied, are ROM E1531 (Berry & Thompson 1962), BM 69114, AM D9984 and AM D27860 (Bayliss 1969a), BM 88503 (Bayliss 1977), and AM 27860 (Pratt & Bayliss 1980). Specimen numbers with their localities are listed in Table 2, and the same order is also used in Table 3.

These nine specimens of ullmannite were chemically analyzed for eight elements (Fe, Co, Ni, S, As, Sb, Bi and Se) by electron microprobe. The following standards were used: Fe, Co, Ni, As, Sb, Bi, FeS, FeS₂, CoS₂, NiS, Sb₂S₃, As₂S₃, (Ni,Co)As₃, FeAsS and Cu₃Se₂. The As standard was repolished and recoated to avoid oxidation. The data were refined with a modified version of the computer program SLAVE (Nicholls *et al.* 1977). Detection limits were determined to be about 0.05 wt.%. The quality of both the Bi and Se determinations may be poor, since the accuracy of the correction factors has not been adequately tested. The analytical results are presented in Table 3, and the rows are ordered to reflect increasing amounts of As.

Calculation of the stoichiometry from the electron-microprobe data in Table 3 based upon a $4MX_n$ structural formula shows that *n* varies between 1.97 and 2.04. Since the data contain both random and systematic errors, no evidence is available to indicate deviations from the stoichiometric proportion $4MX_2$.

In ullmannite NiSbS, the electron-microprobe data in Table 3 show replacement of Ni by up to 0.2% Fe and 3.8% Co. A heterogeneous variation is shown in the Co and Fe replacement of Ni by up to 1.3% Co in specimen BM 85545 and by up to 0.4% Co and 0.1% Fe in specimen BM 28177. The amount of S in the NiSbS formula is almost constant at S_{1.0}, with As replacement up to 0.5%. The amount of Sb in the NiSbS formula is variable, with replacement by up to 10.3% As and 4.6% Bi. A heterogeneous variation is shown in the As replacement of S and Sb by up to 3% As in specimens ROM E1531 and

TABLE 2. UNIT-CELL VALUES, REFLECTION PROFILE, AND LOCALITIES OF NINE ULLMANNITE SPECIMENS

Specimen Number	Unit-Cell <i>aA</i>	Back-Reflection Profile	Locality
Co _{0.1} Ni _{0.9} SbS	5.926	sharp	synthetic
NiSbS	5.935	sharp	synthetic
NiSb _{0.8} As _{0.2} S	5.899	sharp	synthetic
BM 42791	5.925(5)	sharp	Monte Narbo, Sanbus, Sardinia, Italy
AM D27860	5.920(5)	sharp	Broken Hill, N.S.W., Australia
BM 85545	5.922(1)	sharp	Broken Hill, N.S.W., Australia
BM 1909,524	5.933(2)	sharp	New Brancepeeth Colliery Co., Durham, England
BM 88503	5.910(2)	broad	Petersbach, Hamm, Westphalia, Germany
BM 28177	5.922(5)	broad	Petersbach, Hamm, Westphalia, Germany
AM D9984	5.894(2)	broad	Petersbach, Siegen, Germany
ROM E1531	5.909(5)	broad	Obersdorf, Siegen, Germany
BM 69114	5.876(1)	broad	Hartzgerode, Hartz Mountains, Germany

TABLE 3. CHEMICAL COMPOSITION* OF NINE ULLMANNITE SPECIMENS

Specimen Number	Fe	Co	Ni	S	As wt. %	Sb	Bi	Se	Total	Fe	Co	Ni	Molecular %					
													S	As	Sb	Bi		
Co _{0.1} Ni _{0.9} SbS	2.8	24.8	15.1		57.3				100.0		0.10	0.90	1.00		1.00			
NiSbS		27.6	15.1		57.3				100.0			1.00	1.00		1.00			
NiSb _{0.8} As _{0.2} S		28.9	15.8		7.4	47.9			100.0			1.00	1.00	0.20	0.80			
BM 62791	0.7	26.5	14.7	0.4	57.5		0.2	100.0		0.03	0.97	0.98	0.01	1.01				
AM D27860	3.8	23.3	14.8	0.5	57.3			99.7		0.14	0.86	0.99	0.01	1.00				
BM 85545	3.3	24.2	14.9	0.6	57.6			100.6		0.12	0.88	0.98	0.02	1.00				
BM 1909,524	0.2	27.3	15.0	0.8	56.2			99.5		0.01	0.99	1.00	0.02	0.98				
BM 88503	0.8	27.2	15.3	4.0	51.2	0.7		99.2		0.03	0.97	1.00	0.11	0.88	0.01			0.01
BM 28177	0.1	0.5	27.4	15.3	4.8	50.5	2.5	101.1		0.02	0.98	0.99	0.13	0.86	0.02			
AM D9984	0.4	27.7	15.4	5.3	48.8	1.3		98.9		0.01	0.99	1.00	0.15	0.84	0.01			
ROM E1531	0.1	0.7	27.7	15.4	6.3	45.1	4.6	99.9		0.02	0.98	1.00	0.18	0.77	0.05			
BM 69114	0.2	0.4	27.9	15.4	10.3	45.3		99.5	0.01	0.02	0.97	0.97	0.28	0.75				

*Data obtained by electron-microprobe analysis.

BM 69114 and by up to 1.5% As in specimens BM 28177, BM 88503 and AM D9984.

Powder X-ray-diffractometer patterns of ullmannite indicate that the 010 reflection is absent, although the 110 reflection is observed. The absence of the 010 reflection and the presence of the 011 reflection have been confirmed by 114.7 mm Debye-Scherrer powder photographs. The absence of the 010 reflection is confirmed in a calculated pattern obtained with the program of H. Langhof, Institute für Physikalische Chemie, Darmstadt, from the crystal-structure parameters of arsenian ullmannite (Bayliss 1977). The 010 reflection is too low in intensity to be observed, because the calculated relative intensity is 0.07 on a scale of 100. Neither powder X-ray diffraction patterns nor Debye-Scherrer powder photographs show the reflections to be split.

From each specimen of ullmannite, an approximately 50 μ m well-developed equidimensional cube, form {100}, was selected. The preliminary alignment along an a axis was made on a precession camera using unfiltered Mo radiation. These $hk0$ and $h0l$ precession photographs confirm the presence of the 110, 101 and 011 reflections, but also show very weak 100, 010 and 001 reflections.

Eight of these specimens of ullmannite were selected for study by single-crystal diffractometry. Each specimen was accurately centred on a manual four-circle diffractometer with the 800, $\bar{8}00$ and 080 reflections so that an a axis coincides with the diffractometer ϕ axis. For each of the ullmannite specimens, the angular position of about ten strong reflections at high 2θ was measured. No deviation was detected from $a = b = c$ and $\alpha = \beta = \gamma$.

Integrated intensities of 30 reflections, which include 12 reflections forbidden by space-group $P2_13$, were collected with MoK α radiation and a graphite 0002 monochromator. Reflections were scanned in a $\theta:2\theta$ mode at $1^\circ 2\theta$ per minute over a 2° scan width. Background counts were measured for 10 seconds at both the beginning and end of each reflection scan, except if the total counts of a reflection are less than 500; in those cases, in order to obtain better integrated intensities, the background

counts were measured for 60 seconds at both the beginning and end of each reflection scan. A standard 020 reflection, which was measured every 30 reflections throughout the data collection, showed satisfactory experimental stability, so that no correction was applied for instrumental drift. These integrated intensities were corrected for background

TABLE 4. OBSERVED RELATIVE INTENSITIES, STRENGTH OF OPTICAL ANISOTROPISM, AND MOLECULAR % OF (Co,Fe)AsS IN EIGHT SPECIMENS OF ULLMANNITE

hkl	* 1909, 62791, 28177, 85545, E1531, 69114, 88503							
	27860	524	62791	28177	85545	E1531	69114	88503
010	1	0.3(5)	1.5(2)	0	0.1(1)	0	1	3
100	2	0	2	0	0	0	1	3
001	1	0	1	0	0	0.3(5)	0.5(3)	2
030	2	0.1(3)	0.1(3)	1	0.1(1)	0	0	2
300	1	0	1	0	0	0	0	3
003	1	0	0	0	0	0.0(3)	0.2(1)	6
050	0	0	0	0	0.0(1)	1	2	3
500	5	1	1	1	2	0	1	7
005	4	1	0	0	0	1	0.2(1)	1
070	0	0	0	0	0.0(1)	0	1	1
700	0	0	1	0	0	0	0	1
007	0	0	0	0	0	0	0.2(1)	1
110	272	193	241	200	197	210	174	207
011	145	196	145	177	228	133	198	81
101	209	188	207	155	81	152	112	135
210	457	426	498	441	357	480	428	412
021	246	488	332	473	519	341	482	224
102	440	442	373	364	170	311	279	285
120	1000	1000	1000	1000	1000	1000	1000	1000
012		885	546	682	951	623	913	418
201	841	940	897	794	390	882	581	623
310	151	130	174	127	95	137	118	140
031	79	164	117	141	167	103	142	92
103	141	136	119	108	56	91	94	74
130	33	24	24	16	15	17	26	39
013	20	16	12	12	18	14	13	17
301	14	12	18	15	10	19	12	13
330		97	129	93	101	99	88	
033		99	85	83	120	62	98	
303		97	105	79	49	67	60	
Opt.	nil	very weak	very weak	very weak	very weak	very weak	weak	weak
mol. %	1	1	1	2	2	2	3	3

and scaled so that the maximum observed relative intensity (I) is 1000.

The crystallographic axes of each specimen were chosen so that I_{120} is 1000. The columns in Table 4 are ordered according to increasing strength of optical anisotropism. Each column in Table 4 has been arranged in sets of three reflections, which are equivalent in the cubic space-group $P2_13$. The crystal structure of specimens marked by an asterisk in Table 4 has been refined, and the results published (Bayliss 1977, Pratt & Bayliss 1980). Integrated intensities of some $h00$ reflections with $h = 2n + 1$ were collected at 11 different positions about the scattering vector. Where all 11 measured intensities are positive, the lowest intensity is quoted to one decimal place in Table 4, together with the value of 3σ in brackets. For specimen BM 88503, integrated intensities were collected for the 100 reflection at $1/2^\circ$ intervals over a 180° range about the scattering vector. All 361 measured intensities are positive, and the lowest intensity was observed at the value of 2.4 σ .

The F_{obs} values for F_{120} , F_{012} and F_{201} of specimens BM 88503 (Bayliss 1977) and AM 27860 (Pratt & Bayliss 1980) are approximately equal. The variability in the values of I_{120} , I_{012} and I_{201} in Table 4 for the eight specimens of ullmannite involves a factor of about two, which takes into account the fact that these observed relative intensities have not been corrected for absorption. Therefore, it is not essential to correct all the relative intensities for absorption and to calculate their standard deviations.

DISCUSSION

Since King & Prewitt (1979) found that one out of every three measurements is zero or less and hence not affected by the Renninger effect, 11 measurements should be sufficient to find a single position not affected by the Renninger effect. The presence of some $h00,0k0$ and $00l$ reflections observed in precession photographs is confirmed by results in Table 4, as these reflections are observed above the 3 σ confidence level.

Table 2 lists the unit-cell values calculated from a Debye-Scherrer photograph and indicates whether the reflections near $\theta = 90^\circ$ are sharp or broad. The specimens with minor As are characterized by sharp back-reflections and accurate unit-cell values, whereas the specimens with major As are characterized by broad back-reflections and less accurate unit-cell values. The correlation between the accuracy of the unit-cell values and the back-reflection profile is attributed to heterogeneous replacement of Sb by As. Both the Ni-Co and As-Sb variations in Table 3 fall within the solid-solution limits at 550°C (Bayliss 1969b). The measured unit-cell values of natural bismuth-free ullmannite in Table 2 lie within 0.002 Å of the predicted values from the chemical com-

position in Table 3 and the unit-cell values of synthetic ullmannite (Bayliss 1969b).

All reflections, which were recorded by single-crystal and powder diffractometers and on Debye-Scherrer and precession photographs, may be indexed on a cubic unit-cell with a between 5.88 and 5.93 Å, which is similar to the unit-cell values of synthetic ullmannite determined by Bayliss (1969b) and quoted in Table 2. No deviation from $a = b = c$ and $\alpha = \beta = \gamma$ was detected.

Most specimens observed under a reflecting microscope show optical anisotropism, which is recorded in Table 4. These results are similar to those of Klemm (1962). The strength of the optical anisotropism shows a correlation with the reflections forbidden by cubic space-group $P2_13$ ($h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd), which are recorded in Table 4. Specimens with weak anisotropism show weak reflections forbidden in cubic space-group $P2_13$, including reflections 700, 070 and 007. In contrast, specimens with very weak anisotropism show some weak reflections forbidden in cubic space-group $P2_13$, but excluding reflections 700, 070 and 007.

Ullmannite, with the end-member formula of NiSbS, has three sets of four atomic sites identically occupied, because Sb is significantly larger than S and there is negligible solid-solution between Sb and S (Bayliss 1969b). Since there is no apparent chemical reason to lower the symmetry, ullmannite with the end-member formula of NiSbS is probably cubic in space-group $P2_13$.

Substitutions noted in ullmannite are Co and Fe for Ni, As and Bi for Sb, and As for S (Table 3). Since As is significantly smaller than Sb, and Bi is significantly larger than Sb, either As or Bi could be ordered in one or more of the four atomic sites normally occupied by Sb. Since As is significantly larger than S, As could be ordered in one or more of the four atomic sites normally occupied by S. At high temperatures of mineral formation, the atoms

TABLE 5. OBSERVED AND CALCULATED STRUCTURE FACTORS

hkl	BM 27860	BM 88503		hkl
	F_{obs}	F_{obs}	F_{calc}	
010	4.2(1)	3	3	010
001	1.7(1)	2	3	100
100	5.0(1)	4	1	001
030	4.1(3)	4	2	030
003	9.7(5)	9	3	300
300	3.3(5)	4	1	003
050	12(2)	12	2	050
005	2(4)	3	1	500
500	12(2)	15	2	050
		4	2	070
		3	2	700
		4	2	007

would be disordered over the four atomic sites, whereas at low temperatures of mineral formation, atomic ordering could occur. Arsenian ullmannite BM 88503 is partly ordered, with preferential occupancy of the atomic site S_3 by $As_{0.05}$ and the atomic site Sb_4 by $As_{0.20}$. The crystal-structure refinement shows a small but significant drop of R_w from 4.3 for a cubic space-group $P2_13$ model to 3.8 for a pseudocubic space-group $P1$ model (Bayliss 1977).

The small but significant deviation of the crystal structure of specimen BM 88503 from cubic symmetry is shown by the reflections forbidden in cubic space-group $P2_13$, recorded in Table 4. Because all the other specimens in Table 4 have weaker reflections forbidden by cubic space-group $P2_13$ than those of BM 88503, deviations from cubic symmetry are unlikely to be detected in any specimen listed in Table 4 by further crystal-structure refinement, of specimen AM 27860 (Pratt & Bayliss 1980) for example. Therefore, any further attempt to refine the crystal structure of these specimens to prove As ordering is unlikely to be successful.

There are problems with a simple ordering-scheme for As: other minerals in the pyrite group are either completely ordered (space groups $Pca2_1$ or $P2_13$) or disordered (space group $Pa3$), and no other partly ordered member of the pyrite group has been documented. The F_{obs} values of BM 88503 are significantly greater than the F_{calc} of the reflections forbidden by cubic space-group $P2_13$, as shown by Table 5, which suggests that the crystal-structure model has a systematic error. The wide range of As content from 0.4 to 10.3 wt. % in ullmannite shown by Table 3 is not reflected by the intensity of the forbidden reflections in cubic space-group $P2_13$, which have similar low intensities as shown by Table 4. Table 5 shows that the F_{obs} of reflections forbidden by cubic space-group $P2_13$ in cobaltian ullmannite (BM 27860) are similar to the F_{obs} for arsenian ullmannite (BM 88503) after reordering the reflections with a different but acceptable orientation.

In contrast to the type of ordering of the Sb-S pair in ullmannite (Fig. 1), with a cubic space-group $P2_13$, (Co,Fe)AsS has a different type of ordering of the As-S pair (Fig. 1), with an orthorhombic space-group $Pca2_1$ (e.g., cobaltite, cobaltian gersdorffite). The amount of (Co,Fe)AsS in the ullmannite specimens (Table 3) varies from 1 to 3 mol. % (Table 4); however, specimens BM 88503 and BM 69114, with 3 mol. % of (Co,Fe)AsS, show weak optical anisotropism, whereas the other ullmannite specimens, with only 1 to 2 mol. % of (Co,Fe)AsS, show very weak optical anisotropism (Table 4). Therefore, the strength of the optical anisotropism shows a correlation with the amount of (Co,Fe)AsS as well as with the intensity of reflections forbidden by cubic space-group $P2_13$. The fine lamellae

observed in ullmannite by Ramdohr (1980) suggest the presence of twinning. Such a sextuplet (Fig. 1) of interpenetrating, twin-related, orthorhombic space-group $Pca2_1$ domains in (Co,Fe)AsS about a $\bar{3}$ twin axis [111] within the cubic space-group $P2_13$ crystal structure of ullmannite would explain the observations.

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REFERENCES

- BAYLISS, P. (1969a): X-ray data, optical anisotropism, and thermal stability of cobaltite, gersdorffite, and ullmannite. *Mineral. Mag.* **37**, 26-33.
- _____ (1969b): Isomorphous substitution in synthetic cobaltite and ullmannite. *Amer. Mineral.* **54**, 426-430.
- _____ (1977): Crystal structure refinement of arsenian ullmannite. *Amer. Mineral.* **62**, 369-373.
- _____ (1982a): A further crystal structure refinement of cobaltite. *Amer. Mineral.* **67**, 1048-1057.
- _____ (1982b): A further crystal structure refinement of gersdorffite. *Amer. Mineral.* **67**, 1058-1064.
- _____, BERRY, L.G., MROSE, M.E., SABINA, A.P. & SMITH, D.K. (1983): *Group Data Book, Mineral Powder Diffraction File*. Joint Committee on Powder Diffraction Standards, Swarthmore, Pa.
- BERRY, L.G. & MASON, B. (1959): *Mineralogy: Concepts, Descriptions and Determinations*. W.H. Freeman, San Francisco.
- _____ & THOMPSON, R.M. (1962): X-ray powder data for ore minerals: the Peacock Atlas. *Geol. Soc. Amer. Mem.* **85**.
- BOKII, G.B. & TSINOBEV, L.I. (1954): X-ray examination of cobaltite, gersdorffite and ullmannite. *Trudy Inst. Krist. Akad. Nauk SSSR* **9**, 239-250 (in Russ.) [*Chem. Abstr.* **48**, 13553h].
- CABRI, L.J., HARRIS, D.C., STEWART, J.M. & ROWLAND, J.F. (1970): Willyamite redefined. *Aust. Inst. Mining Metall. Proc.* **233**, 95-100.
- ENTNER, P. & PARTHÉ, E. (1973): PtGeSe with cobaltite structure, a ternary variant of the pyrite structure. *Acta Cryst.* **B29**, 1557-1560.
- EVANS, B.J., BAYLISS, P., JOHNSON, R.G. & CECIL, C.B. (1982): ^{57}Fe Mössbauer spectroscopy of anisotropic pyrites. In Proc. Inorganic Constituents in Coal Meeting (Boiling Springs, Pa.) (abstr.)

- FINKLEA, S.L., III, CATHEY, L. & AMMA, E.L. (1976): Investigation of the bonding mechanism in pyrite using the Mössbauer effect and X-ray crystallography. *Acta Cryst.* **A32**, 529-537.
- FLEISCHER, M. (1983): *Glossary of Mineral Species*. The Mineralogical Record, Tucson, Arizona. Additions and Corrections. *Mineral. Record* **15**, 51-54 (1984).
- KING, H.E., JR. & PREWITT, C.T. (1979): Structure and symmetry of CuS_2 (pyrite structure). *Amer. Mineral.* **64**, 1265-1271.
- KLEMM, D.D. (1962): Anisotropieeffekte bei kubischen Erzmineralien. *Neues Jahrb. Mineral. Abh.* **97**, 337-356.
- NICHOLLS, J.W., FIESINGER, D.W. & ETHIER, V.G. (1977): Fortran IV programs for processing routine electron microprobe data. *Computers Geosci.* **3**, 49-83.
- PAULING, L. (1978): Covalent chemical bonding of transition metals in pyrite, cobaltite, skutterudite, millerite and related minerals. *Can. Mineral.* **16**, 447-452.
- PEACOCK, M.A. & HENRY, W.G. (1948): The crystal structure of cobaltite (CoAsS), gersdorffite (NiAsS), and ullmannite (NiSbS). *Univ. Toronto Studies Geol. Ser.* **52**, 71-80.
- PRATT, J.L. & BAYLISS, P. (1980): Crystal structure refinement of a cobaltian ullmannite. *Amer. Mineral.* **65**, 154-156.
- RAMDOHR, P. (1980): *The Ore Minerals and Their Intergrowths*. Pergamon Press, Oxford.
- RAMSDELL, L.S. (1925): The crystal structure of some metallic sulphides. *Amer. Mineral.* **10**, 281-304.
- TAKÉUCHI, Y. (1957): The absolute structure of ullmannite (*sic*), NiSbS . *Mineral. J. Japan* **2**, 90-102.
- TOSSELL, J.A., VAUGHAN, D.J. & BURDETT, J.K. (1981): Pyrite, marcasite, and arsenopyrite type minerals: crystal chemical and structural principles. *Phys. Chem. Minerals* **7**, 177-184. .

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