CLINOSAFFLORITE : A MONOCLINIC POLYMORPH OF SAFFLORITE

DENNIS RADCLIFFE

Department of Geology, University of Georgia, Athens

L.G. BERRY

Department of Geological Sciences
Queen's University, Kingston, Ontario

ABSTRACT

Clinosafflorite is monoclinic. The sub-cell (corresponding to the safflorite orthorhombic cell) with $a = 5.040\text{Å}$, $b = 5.862\text{Å}$, $c = 3.139\text{Å}$, $\beta = 90°13'$, contains 2 $[Co_{0.76}Fe_{0.14}Ni_{0.10}As_2]$ with D (calc) = 7.46. The apparent space group from indexed powder data is $P2_1/n$. The true cell, established for $CoAs_2$, with a and c doubled is B-centred monoclinic.

Clinosafflorite, found in three specimens from Cobalt, Ontario, is intimately intergrown with skutterudite. Microprobe analyses of three specimens give a range of metal composition Co(0.70-0.76) Fe(0.14-0.26) Ni(0.01-0.10). Indexed powder data show that a decreases and b increases with increasing cobalt. The optical properties are very close to those of safflorite.

Safflorite, from the Nipissing mine, Cobalt with very similar composition, is also intergrown with skutterudite. Clinosafflorite and safflorite, close to the composition $Co_{0.75}Fe_{0.15}Ni_{0.10}As_2$, are polymorphic.

Analyses of natural specimens of non-cubic diarsenides of the transition metals (Radcliffe & Berry 1968) show a complete range of solid solution between $FeAs_2$ and $CoAs_2$ with substitution of $NiAs_2$ up to 30 mole percent. Loellingite is $FeAs_2$ with some substitution of $CoAs_2$ but no significant substitution of $NiAs_2$. Safflorite is $(Co,Fe,Ni)As_2$. Loellingite and most natural safflorite specimens are orthorhombic with space group *Pnnm*. Studies of synthetic material from the $FeAs_2 - CoAs_2 - NiAs_2$ system (Heyding & Calvert 1960, Quesnel & Heyding 1962, Swanson *et al.* 1960, 1966, Roseboom 1963, Radcliffe & Berry 1968) confirm the orthorhombic symmetry for loellingite and most safflorites, but they also show that material with 80 - 100 mole percent $CoAs_2$ is monoclinic. Darmon & Wintenberger (1966) in a single crystal study of $CoAs_2$ confirm the monoclinic symmetry of $CoAs_2$. Naturally occurring monoclinic safflorite has not been previously reported although Peacock (1944) suggested monoclinic symmetry for a Nordmark safflorite specimen. This suggestion led later authors (Heyding & Calvert 1960, Swanson *et al.* 1960) to assign monoclinic symmetry to all safflorite. Re-examination of Peacock's films (*h0l* and *h1l* Weissenberg films, Cu*K*α radiation) reveals the presence of very weak reflections for 003 and 012, but no positive evidence for monoclinic symmetry. Some minor differences in intensities for equivalent reflections in orthorhombic symmetry are, at least in part, due to the presence of areas of high absorption in the Weissenberg films. Analyses by microprobe, of a Nordmark safflorite specimen from the locality studied by Peacock (1944) give a composition closer to loellingite (16 – 17 mole percent $CoAs_2$) than was assumed by Peacock from older analyses. Available data indicates that iron - rich safflorites have orthorhombic symmetry. Swanson *et al.* (1960) indexed powder data for synthetic $CoFeAs_4$ as monoclinic with $\beta = 90°$ but with no indices incompatible with the orthorhombic space group *Pnnm*.

Naturally occurring monoclinic safflorite has been recognized by the authors in three specimens from the Cobalt area, Ontario, Canada. The name clinosafflorite is proposed for this monoclinic phase. This proposal was approved on June 2, 1970 by the Commission on New Minerals and Mineral Names (IMA) by a vote of 16 to 3. Clinosafflorite is finely intergrown with skutterudite, $(Co,Fe,Ni)As_{3-x}$, in the three specimens. The composition of clinosafflorite, determined by microprobe (using Co, Fe, Ni, As and FeS_2 as standards) is included in Table 1. Other safflorite specimens with closely similar compositions have orthorhombic symmetry, hence clinosafflorite is a monoclinic polymorph of safflorite. Typical powder diffraction data for clinosafflorite is given in Table 2. The optical properties are very close to those of safflorite; they could not be determined accurately because of the fine intergrowth with skutterudite.

Using the setting of loellingite and safflorite the true unit-cell of synthetic $CoAs_2$ has *a* and *c* doubled and $\beta = 90° 30'$. This cell is *B*-centered monoclinic and contains $8[CoAs_2]$. The primitive cell with $a' = ½[101]$, $b' = b$, $c' = ½[\bar{1}01]$, $\beta \approx 117°$ and $Z = 4$ has the space group $P2_1/a$ (Swanson *et al.* 1966) or $P2_1/c$ (Darmon & Wintenberger 1966). The correct designation of the glide plane is uncertain (Table 1). The determination of the glide plane by Swanson *et al.* (1966)* is based on the indexing of one powder line ($d = 2.045$).

Darmon & Wintenberger (1966), in a Weissenberg study of synthetic $CoAs_2$ crystals, confirmed the monoclinic cell dimensions described above but derive a space group $P2_1/c$ in their setting with $a > c$. The direction of the glide is thus in conflict with that given by the Swanson *et al.* (1966) indexing. Wintenberger (priv. comm.) reports that the precision

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* Swanson *et al.* (1966) give their data in terms of the *P* monoclinic cell with $a < c$ and $P2_1/c$, their data is quoted here with *a* and *c*, and *h* and *l* interchanged.

of b and c (pseudo-orthorhombic cell) is good but a and β are less precise since only low angle reflections from Weissenberg diagrams of twinned crystals were available. Resolution of this problem must await the availability of better crystals.

Clinosafflorite suitable for single crystal study has not been found, furthermore the difficulty of obtaining a pure sample free from traces of skutterudite and calcite precludes the recognition of the weak lines*

TABLE 1. SAFFLORITE AND CLINOSAFFLORITE : LATTICE DIMENSIONS

Safflorite Orthorhombic	a	b	c	β	
$CoFeAs_4$	5.232	5.952	2.957	90°00′	Swanson *et al.* (1960)
Nordmark, Sweden $Co_{0.16}Fe_{0.84}As_2$**	5.259	5.970	2.919	—	Radcliffe (1966)
Cobalt, Ontario $Co_{0.55}Fe_{0.41}Ni_{0.04}As_2$	5.173	5.954	2.999	—	Radcliffe (1966)
Nipissing mine, Cobalt 1B63 $Co_{0.74}Fe_{0.18}Ni_{0.08}As_2$	5.1869 ±.0002	5.8924 ±.0002	3.0530 ±.0002	—	Radcliffe
Clinosafflorite, Monoclinic, Synthetic $CoAs_2$					
Pseudo-orthorhombic $B2_1/-$	2 × 5.048	5.872	2 × 3.127	90°28½′	Swanson *et al.* (1966)
Monoclinic $P2_1/a$	5.960	5.872	5.916	116°27′	
Pseudo-orthorhombic $B2_1/-$	2 × 5.06	5.86	2 × 3.12	90°36′	Darmon & Wintenberger (1966)
Monoclinic $P2_1/c$	6.03	5.86	5.92	117°—	
Pseudo-orthorhombic $B2_1/-$	2 × 5.072	5.873	2 ×3.131	90°34′	Radcliffe (1966)
Monoclinic $P2_1/-$	5.986	5.873	5.934	116°41½′	
$Co_{0.87}Ni_{0.13}As_2$ $B2_1/-$	2 × 5.0383	5.8637	2 × 3.1599	90°13′	Roseboom (1963)
$P2_1/-$	5.957	5.8637	5.934	115°48½′	
Clinosafflorite, Cobalt, Ontario (pseudo-orthorhombic, in safflorite setting)					
$Co_{0.76}Fe_{0.14}Ni_{0.10}As_2$	5.040 ±.004	5.862 ±.004	3.139 ±.003	90°13′ ±2′	IB20
$Co_{0.73}Fe_{0.26}Ni_{0.01}As_2$	5.062 ±.018	5.851 ±.008	3.149 ±.008	90°18′ ±8′	IB52
$Co_{0.70}Fe_{0.21}Ni_{0.09}As_2$	5.121 ±.010	5.847 ±.052	3.094 ±.005	90°17′ ±4′	IB83

* Lines which require doubling of a and c in the loellingite-type cell with *Pnnm*.

** Compositions given in mole percent.

measured by Swanson *et al.* (1966). The doubling of all lines, indexed as *h0l* or *hkl* in the loellingite cell, clearly requires a monoclinic lattice, but all lines can be indexed with a lattice of loellingite type (Table 2).

The reasons for the symmetry change may be the result of differing thermal histories perhaps affected by associated phases. Geometrically the effect can be described in terms of ligand field theory. In $CoAs_2$ paramagnetic susceptibility measurements (Powell 1967) indicate a low spin configuration of the 5 non-bonded 3*d* orbital electrons of cobalt in octahe-

TABLE 2. CLINOSAFFLORITE AND SAFFLORITE : POWDER DIFFRACTION DATA
Diffractometer $CuK\alpha_1 = 1.54050$Å

Clinosafflorite 1B20 Cobalt				Safflorite 1B63 Cobalt			
$a = 5.040$, $b = 5.862$, $c = 3.139$, $\beta = 90°13'$				$a = 5.1869$, $b = 5.8924$, $c = 3.0530$			
$Co_{0.76}Fe_{0.14}Ni_{0.10}As_2$				$Co_{0.74}Fe_{0.18}Ni_{0.08}As_2$			
I/Io	*hkl*	*d meas.*	*d calc.*	*I/Io*	*hkl*	*d meas.*	*d calc.*
10	020	2.932	2.931				
40	$\bar{1}01$	2.671	2.669	20	101	2.6398	2.6311
40	101	2.657	2.660				
100	120	2.531	2.534	100	120*	2.5829	2.5618
80	$\bar{1}11$	2.427	2.429	10	111	2.4024	2.4024
80	111	2.422	2.422				
20	210	2.313	2.315	90	210	2.3737	2.3737
30	$\bar{2}11$	1.865	1.866	80	211**	1.8638	1.8739
30	211	1.861	1.860				
30	031	1.656	1.659	10	031	1.6518	1.6518
10	$\bar{2}21$	1.636	1.634	10	221	1.6377	1.6414
10	221	1.631	1.630				
5	$\bar{1}31$	1.576	1.577	5	131	1.5739	1.5739
5	131	1.570	1.575				

* Affected by skutterudite 310, *d* = 2.592
** Affected by skutterudite 420, *d* = 1.835
excluded from cell edge computation.

dral configuration with arsenic. Four electrons are spin paired in the t_{2g} orbitals within the As_6 octahedral field of a single unit cell. The fifth electron is spin paired across shared octahedral edges and between neighboring unit cells parallel with the *c* axis. The resulting polycation bonds produce alternating long and short Co–Co distances, parallel with *c*, of 2.77 and 3.47 Å (Darmon & Wintenberger 1966). This alternating attraction and repulsion of Co atoms parallel with *c* leads to a distortion of successive unit cells and produces a monoclinic character.

In synthetic material this monoclinic character has been observed in $CoAs_2$ and in $(Co,Ni)As_2$ with Co:Ni = 7:1. Synthetic composition $Co_{0.8}Fe_{0.2}As_2$ is not measurably monoclinic on powder diffraction patterns and the measurable change of orthorhombic to monoclinic symmetry probably occurs about $Co_{0.9}Fe_{0.1}As_2$. In the natural systems monoclinic character has been observed in more iron rich compositions. However, these compositions also contain Ni. Presumably the combination of Ni (6 non-bonded 3*d* electrons) and Fe (4 non-bonded 3*d* electrons) in the dominantly $CoAs_6$ octahedral field tends to cancel opposing effects. This produces a flux effect of more nearly 5 non-bonded 3*d* electrons *i.e.* the 3*d* orbital characteristic of Co surrounded by an As_6 octahedral field.

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Manuscript received January 1970, emended October 1970.