CRYSTAL STRUCTURE OF RICKARDITE, $Cu_{4-x}Te_2$[1]

S. A. Forman[2] and M. A. Peacock[3]
University of Toronto, Toronto, Canada

Abstract

Rickardite and the identical artificial compound $Cu_{4-x}Te_2$ have the *C*38-type (Cu_2Sb) of structure. Tetragonal, *P*4/*nmm*; $a=3.97$, $c=6.11$ kX; 2Cu in (*a*): 000, $\frac{1}{2}\frac{1}{2}0$; $(2-x)$Cu in (*c*):$0\frac{1}{2}z_1$, $\frac{1}{2}0\bar{z}_1$ with $z_1=0.27\pm0.01$; 2Te in (*c*):$0\frac{1}{2}z_2$, $\frac{1}{2}0\bar{z}_2$, with $z_2=0.715\pm0.005$. The structure is grossly defective, with x nearly constant and equal to 1.2 or roughly 1. The formula Cu_4Te_3 hitherto given for rickardite and for the artificial compound should therefore be replaced by the cell formula or, for simplicity, by Cu_3Te_2. The variously blue colours of rickardite and other copper ores containing Cu^{II} is attributed to Cu atoms in the higher than normal valence state.

Rickardite[4] is a natural copper telluride which was discovered in the ore of the Good Hope Mine, Vulcan, Gunnison County, Colorado, by Dr. Loui Weiss, and was subsequently named and described by Ford (1903). The mineral is massive and brittle, with hardness $3\frac{1}{2}$ and specific gravity 7.54. It has metallic lustre and a remarkable purple-red colour on freshly fractured surfaces. Duplicate analyses indicated the composition Cu_4Te_3. At Vulcan, rickardite is associated with tellurium, petzite, berthierite, and pyrite. The mineral has also been reported at the Empress Josephine mine, Bonanza, Colorado (Patton, 1916, p. 108), the San Sebastian mine, Salvador (Wuensch, 1917, p. 348), the Junction mine, Warren, Arizona (Crawford, 1930, p. 272), the Kalgurli mine, Kalgoorlie, Western Australia (Stillwell, 1931, p. 186), and the Horne mine, Noranda, Quebec (Price, 1934, p. 132); but these reports contain no significant addition to the meagre description of the mineral.

Polished sections of rickardite have been described by Ramdohr (1937, p. 204) and Short (1940, p. 113). Ramdohr remarks that the formula Cu_4Te_3 is not certain and that the composition might be Cu_3Te_2, by analogy with the mineral umangite, Cu_3Se_2, which, however, gives a quite dissimilar *x*-ray powder pattern. The reflecting power is moderate, the reflection pleochroism is very strong and striking (carmine-red to violet-grey), and the anisotropism is enormous (canary-yellow to deep brown-red). Some sections are optically isotropic, indicating that rickardite is hexagonal or tetragonal. The curious porous texture of Ramdohr's section and the arrangement of the individual grains indicated that the

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[1] Based on an unpublished M.A. thesis by S. A. Forman: The crystal structure of rickardite, $Cu_{2-x}Te$—*University of Toronto*, 1946.

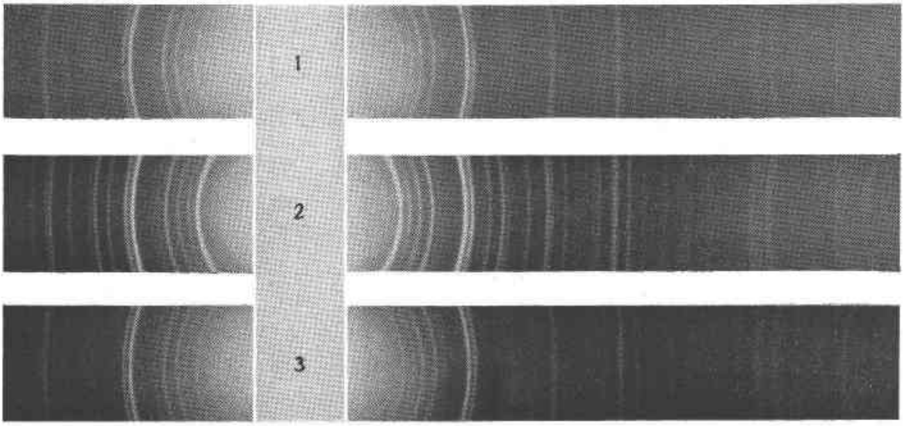
[2] Graduate student and teaching assistant, Department of Geological Sciences.

[3] Professor of Crystallography and Mineralogy, Department of Geological Sciences.

[4] Rickardite and weissite are briefly described by Thompson (1949).

whole mass originated as a pseudomorph of a probably cubic mineral. Short also remarks on the similarity of rickardite and umangite, and he describes four extinctions per revolution between crossed nicols with fiery orange interference colours. *X*-ray information on rickardite is limited to powder spacings and intensities by Waldo (1935, p. 587) and Harcourt (1942, p. 96). Thus rickardite is a mineral of striking and unmistakable appearance; at the same time the description of the mineral is unsatisfactory since it appears to be an inversion product of somewhat uncertain composition and almost unknown crystallography.

Intimately associated with rickardite is a telluride of copper which differs from rickardite in composition and colour. This mineral was distinguished from rickardite by Crawford (1927) who first described it under the name weissite. This second copper telluride is likewise massive, with hardness 3, and specific gravity about 6; it has metallic lustre, a bluish black colour tarnishing deep black, and a composition given by an unusual type of formula Cu_5Te_3. Ramdohr (1938) and Short (1940, p. 113) give observations on polished sections, which are light grey like ordinary chalcocite in reflected light, with practically no reflection pleochroism but distinct anisotropism of orthorhombic character. From the similarity to chalcocite Short suggests that the proper composition of weissite is Cu_2Te. Thus weissite seems to be even less well defined than rickardite and it is not surprising that L. J. S. [pencer] (*Min. Abs.* **3**, 368) considered weissite to be the same as rickardite.



FIGS. 1–3. *X*-ray powder photographs with Cu/Ni radiation; camera radius, $360/4\pi$ mm.; actual size reproductions of contact prints. Fig. 1. Rickardite. Fig. 2. Alloy with Cu: Te=4:3. Fig. 3. Alloy with Cu:Sb=4:3.

The system Cu-Te was studied in detail by Chikashige (1907, in Hansen, 1936, p. 647) without reference to the natural compounds. Two compounds were recognized: Cu_2Te, which takes up to 5% Te in solid solution and apparently passes through two transformations, at 387° and 360°; and Cu_4Te_3, which inverts at 365° to a low temperature form. Watanabe (in Ramdohr, 1938) notes that weissite corresponds to artificial Cu_2Te with 5% added Te; rickardite presumably corresponds to the artificial compound Cu_4Te_3. The results on artificial tellurides appear to support the individuality of both rickardite and weissite. The unusual composition of the former, Cu_4Te_3, seems to be confirmed, while the latter appears to have a defective Cu_2Te composition rather than the definite composition Cu_5Te_3.

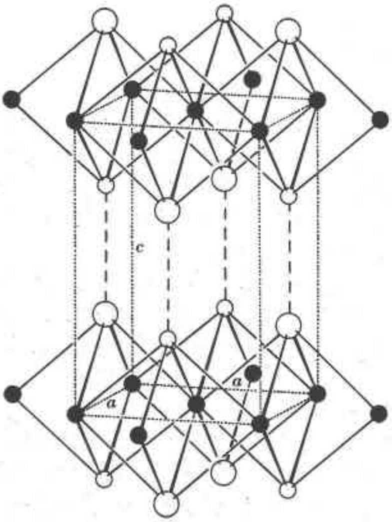


FIG. 4. Rickardite structure; small filled circles are fully occupied Cu positions; small blank circles are partially (roughly half) filled Cu positions; larger blank circles are Te positions.

The present work is concerned only with rickardite, the purple-red mineral with empirical composition Cu_4Te_3. To verify the probable identity of this mineral with the compound Cu_4Te_3 reported in the system Cu-Te, a charge of the powdered elements in the proportions Cu:Te $=4:3$ was fused in an evacuated silica glass tube and cooled in air. The product was a nearly homogeneous platy crystalline product with the characteristic purple-red colour of rickardite and a distinct pinakoidal cleavage parallel to the plates. This product gave an x-ray powder pattern (Fig. 2) which is identical with that of the mineral, (Fig. 1), confirming the presumed identity of rickardite and the artificial compound with the empirical composition Cu_4Te_3. The phase diagram in Hansen (1936, p. 648) indicates that this compound does not vary considerably in composition.

Ramdohr's recognition of the uniaxial character of rickardite proved to be well founded. A study of the spacings of the fairly simple powder pattern led to a tetragonal lattice with relatively small dimensions:[5]

$$a=3.97,\ c=6.11\ \text{kX}$$

On this lattice the powder pattern was completely indexed with good agreement between measured and calculated spacings, as shown later in Table 1. The systematically missing spectra lead to the single condition, $(hk0)$ present only with $(h+k)$ even. This condition is characteristic of the space-groups $P4/n$ and $P4/nmm$, in both of which there are no odd numbers of equivalent positions. From the mean values of the duplicate analyses of rickardite, Cu 40.74, Te 59.21 (Ford, 1903), the measured specific gravity 7.54, the cell dimensions given above, and the mass factor 1.650, the computed cell content is Cu 2.82, Te 2.04 atoms. Clearly the structural formula cannot be Cu_4Te_3, which appeared to be so well established. The ideal cell content must be Cu_4Te_2 and therefore the structural formula must be written $Cu_{4-x}Te_2$ indicating a deficiency in Cu amounting in this case to roughly one atom per unit cell.

Before attempting to determine the atomic arrangement of the copper telluride, the *Strukturbericht* was searched for analogous structures. It was soon found that the structure of the artificial compound Cu_2Sb (*C*38-type, SB, 1937, 33), determined by Elander, Hägg & Westgren (1935), would probably prove to be the arrangement of the copper telluride. Cu_2Sb is tetragonal with the space-group $P4/nmm$, which is one of the two space-groups allowed for $Cu_{4-x}Te_2$; the cell dimensions of Cu_2Sb are:

$$a=3.992,\ c=6.091$$

which are very similar to those of rickardite; the powder intensities of the two compounds are nearly alike, and the antimonide even has a noteworthy violet colour to compare with the purple-red of the telluride.

In the structure of Cu_2Sb the atoms are placed as follows:

2 Cu in (a): $000;\ \frac{1}{2}\frac{1}{2}0$
2 Cu in (c): $0\frac{1}{2}z_1;\ \frac{1}{2}0\bar{z}_1$, with $z_1=0.27$
2 Sb in (c): $0\frac{1}{2}z_2;\ \frac{1}{2}0\bar{z}_2$, with $z_2=0.70$

The structural problem of rickardite thus reduces to finding the distribution of approximately three Cu atoms over the four Cu positions and determining the special values of the two parameters, z_1, z_2.

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[5] Using $\lambda\ CuK\alpha_1=1.5374$ kX.

The three Cu atoms may be distributed over the four Cu positions in the structure of rickardite in only three possible ways which would not degrade the symmetry of the structure:

1) Three Cu atoms distributed statistically over the four positions so that in effect we would have scattering due to $\frac{3}{4}$Cu at each of the four positions.

2) One Cu atom at each of the two positions in (*a*) and the remaining Cu atom distributed over the two positions in (*c*), giving the effect of $\frac{1}{2}$Cu atom in each of the (*c*) positons.

3) One Cu atom in each of the (*c*) positions and the remaining Cu atom distributed over the two positions in (*a*), giving the effect of $\frac{1}{2}$Cu atom in each of the (*a*) positions.

A choice between these three possibilities was made by comparing measured and calculated intensities[6] for (*hk*0) reflections which are unaffected by the variable parameters. The results of this comparison are shown below; it is clear that only the second possibility, namely two Cu atoms in the (*a*) positions and one Cu atom distributed over the (*c*) positions gives calculated values which correspond to those observed on the natural and artificial material.

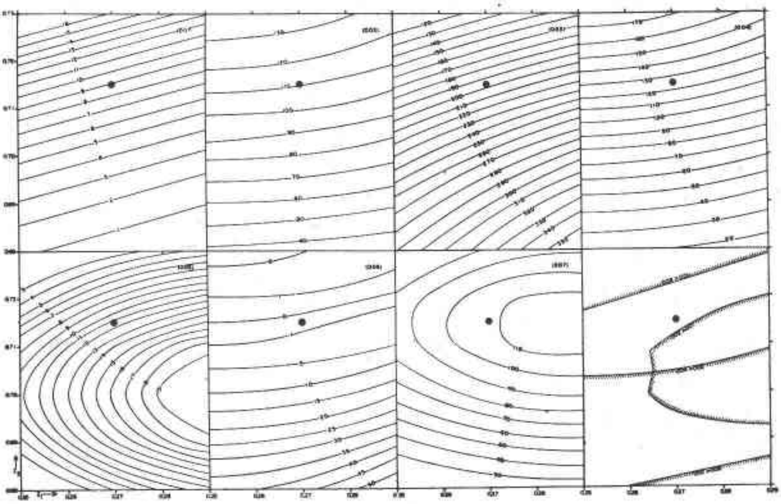

FIG. 5. Calculated intensities of (00*l*) planes with variation of z_1, z_2, to compare with relative Weissenberg intensities.

	(110)	(200)	(220)	(130)
1) 3 Cu in (*a*) and (*c*):	177	197.5	59	27.7
2) 2 Cu in (*a*), Cu in (*c*):	95	197.5	59	15.2
3) Cu in (*a*), 2 Cu in (*c*):	285	197.5	59	43.9
Observed Rickardite:	2	4	2	0
Observed Artificial Compound:	3	5	2	0

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[6] Using $I \propto NLP|F_0|^2$ with f_0 values from *ITDCS* (1935).

For the purpose of determining the two variable parameters, z_1 which applies to the two $\frac{1}{2}$Cu atoms in (*c*) and z_2, the two Te atoms in (*c*), the powder intensities on the natural and artificial materials were supplemented by intensities of (00*l*) reflections given by a minute basal cleavage plate which had been rotated about a random axis in the basal plane. Packing considerations indicated that the parameters to be determined would certainly lie within the ranges $z_1=0.25$ to 0.29, $z_2=0.68$ to 0.73, and therefore these limits were chosen for the computations represented in the contour maps showing the variation of intensity with both parameters for planes of the type (00*l*) (Fig. 5). In the last square of this figure, the areas excluded by the observed relative intensities of the (00*l*) reflections from the crystal plate are fenced off, leaving a permissible region which restricts z_2 fairly definitely but imposes little restriction on z_1.

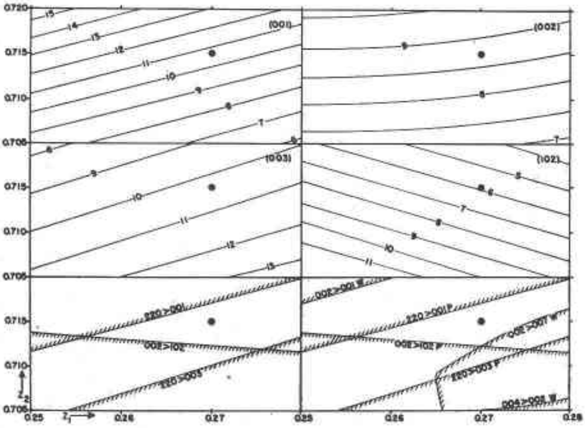

FIG. 6. Calculated intensities of selected planes with variation of z_1, z_2, to compare with certain relative Weissenberg and powder intensities.

In an endeavour to restrict both parameters a little more sharply, a second set of intensity maps was prepared to compare with the powder intensities for planes (00*l*), (002), (003), (102) (Fig. 6). Below these maps the permissible area has been delimited, on the left by certain observed relative powder intensities (*P*) and on the right by two additional single crystal intensities (*W*). In this way z_2 is fixed fairly sharply at 0.715 ±0.005; z_1 is less sharply restricted, the best value being 0.27±0.01. The relatively wide permissible range of z_1 is due to the fact that this is the parameter of the single Cu atom distributed over the (*c*) positions; this atom has only about one-quarter of the scattering power of the two Te atoms fixed by z_2.

These values of z_1 and z_2 give the following comparison of calculated

TABLE 1. RICKARDITE AND ARTIFICIAL $Cu_{4-x}Te_2$: OBSERVED AND CALCULATED SPACINGS AND POWDER INTENSITIES

Tetragonal, $P4/nmm$; $a=3.97$, $c=6.11$ kX

d(meas.)[7]	d(calc.)	(hkl)	I(calc.)[8]	I(obs.)	
				Rickardite[7]	Artif.[8]
6.05	6.110	(001)	1.29	½	2
3.35	3.329	(011)	6.56	6	8
3.03	3.055	(002)	1.07	1	3
2.81	2.807	(110)	2.28	2	3
2.54	2.551	(111)	3.90	4	4
2.42	2.421	(012)	0.73	½	2
2.07	2.067	(112)	10.00	10	10
2.05	2.037	(003)	1.28	1	2
1.984	1.985	(020)	4.80	4	5
—	1.888	(021)	0.18	—	—
1.816	1.812	(013)	0.71	1	2
1.703	1.705	(121)	1.98	2	3
1.665	1.665	(022)	0.71	½	1
—	1.649	(113)	0.07	—	—
1.528	1.535	(122)	0.45	1	2
	1.528	(004)	0.60		
1.421	1.426	(014)	0.41	2	3
	1.422	(023)	1.39		
1.404	1.404	(220)	1.43	2	2
—	1.368	(221)	0.06	—	—
1.339	1.342	(114)	0.10	1	2
	1.338	(123)	0.48		
1.292	1.293	(031)	0.37	½	¼
1.276	1.275	(222)	0.28	—	¼
1.254	1.255	(130)	0.37	½	¼
1.229	1.230	(131)	0.70	½	½
—	1.222	(005)	0.04	—	—
—	1.214	(032)	0.08	—	—
1.209	1.211	(024)	1.09	½	3
—	1.168	(015)	0.03	—	—
1.156	1.161	(132)	2.65	3	5
	1.158	(124)	0.41		
	1.156	(223)	0.70		
1.121	1.120	(115)	1.11	1	2
—	1.110	(033)	0.14	—	—
1.083	1.084	(231)	0.47	1	1
—	1.069	(133)	0.04	—	—
—	1.041	(025)	0.12	—	—
1.034	1.036	(232)	0.11	½	½
	1.034	(224)	0.72		
—	1.018	(006)	0.00	—	—
0.986	0.986	(016)	0.25	—	½

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[7] By R. M. Thompson; routine observations for a standard determinative powder pattern. [8] By S.A.F.

and observed intensities for single crystal (00*l*) reflections:

	(001)	(002)	(003)	(004)	(005)	(006)	(007)
I(calc.)	0.5	5.7	10.0	6.4	0.6	0.01	5.5
I(obs.)	½	5½	10	6	1	vvw	5

To verify the chosen parameters, they were used to compute intensities of all the planes within the range of the powder pattern. The result is shown in Table 1 in which the calculated values are compared with those of the natural and artificial material. The agreement is unusually good and shows that the chosen parameters have been accurately determined.

TABLE 2. RICKARDITE ($Cu_{4-x}Te_2$) AND $Cu_{4-x}Sb_2$: COMPARISON OF STRUCTURAL DATA

	$Cu_{4-x}Te_2$		$Cu_{4-x}Sb_2$
Space-group	*P4/nmm*		*P4/nmm*
a	3.97		3.992
c	6.11		6.091
z_1	0.27		0.27
z_2	0.715		0.70
Cu in (*a*) to 4 Cu in (*a*)	2.81	Cu in (*a*) to 4 Cu in (*a*)	2.82
4 Cu in (*c*)	2.58	4 Cu in (*c*)	2.59
4 Te in (*c*)	2.72	4 Sb in (*c*)	2.70
Cu in (*c*) to 4 Cu in (*a*)	2.58	Cu in (*c*) to 4 Cu in (*a*)	2.59
4 Te in (*c*)	2.81	4 Sb in (*c*)	2.83
1 Te in (*c*)	2.64	1 Sb in (*c*)	2.62
Te in (*c*) to 4 Cu in (*a*)	2.72	Sb in (*c*) to 4 Cu in (*a*)	2.70
4 Cu in (*c*)	2.81	4 Cu in (*c*)	2.83
1 Cu in (*c*)	2.64	1 Cu in (*c*)	2.62

The structure of rickardite is illustrated in Fig. 4 in which the fully occupied Cu positions are shown by solid black circles, the statistically half-occupied Cu positions, by the small blank circles, and the Te positions by the larger blank circles. The shortest atomic connections are shown in the figure and their lengths are listed in Table 2 which gives a full comparison of the structural data of rickardite and the corresponding antimonide of copper. It will be seen that there is very little difference between the two sets of interatomic distances. The corresponding Cu-Cu distances differ by only 0.01 and the Cu-Te distances are 0.02 greater than the corresponding Cu-Sb distances. This close similarity is in keeping with the fact that Te immediately follows Sb in atomic number. As shown in Fig. 4, the structure of rickardite and the corresponding Sb compound is a layer structure in which the close packed layers are relatively weakly connected by the vertical bonds joining the roughly half-filled Cu positions to the Te atoms. This is in keeping with the basal cleavage which is common to both these compounds.

From the close similarity of the structures of rickardite and copper antimonide, it was to be expected that the powder patterns of the two compounds would be nearly alike. In attempting to prepare the copper antimonide, it was discovered that the antimonide apparently also has a defective composition. A fusion with the composition Cu_2Sb gave an intergrowth of the compound previously considered to be pure Cu_2Sb, together with a substantial amount of a second phase. On the other hand, a fusion with the composition Cu:Sb=4:3 gave a purer product, corresponding to rickardite. It may be seen from the powder photographs (Figs. 1, 2, 3) that the powder pattern of this defective copper antimonide $Cu_{2-x}Sb$ closely resembles those of natural and artificial rickardite. Our preparations of the antimonide showed the violet colour mentioned by Elander, Hägg & Westgren and explained by them as probably due to some polarization of the atoms; but this colour is not as arresting as the fiery purple-red of natural and artificial rickardite.

Discussion. Since the unit cell of rickardite and the identical artificial compound contains $Cu_{4-x}Te_2$ with $x\sim1.2$ (30 per cent) the empirical formula Cu_4Te_3 should be replaced by the cell formula; or, for simplicity, the composition could be written Cu_3Te_2, since x is fairly constant and near 1 in amount. Rickardite thus presents the unusual case of a defective structure with a large and almost invariant proportion of vacant metal positions. The ideal composition Cu_4Te_2 is far beyond the existence range of the phase. It is true, the compound Cu_2Te, with only slight deficiency of Cu, is known in the artificial system and as the mineral weissite; but Thompson (1949) has confirmed the fact that this phase is entirely different from the rickardite phase. Thus rickardite differs from the familiar case of pyrrhotite, $Fe_{2-x}S_2$, in which x has a relatively small and continuous range, 0–0.4 (20 per cent); nor can rickardite be compared to the series $Ni_{2-x}Te_2$, in which x ranges continuously from 0 to 1 (50 per cent), giving Ni_2Te_2 (*B*8-type, NiAs) to $NiTe_2$ (melonite, *C*6-type, CdI_2) (Klemm & Fratini, 1943).

The defective composition of rickardite indicates presence of Cu in two valence states, Cu^I and Cu^{II}. The simplified formula Cu_3Te_2 can thus be written $Cu_2Te \cdot CuTe$, and from this it may be inferred that Cu^I fills the (*a*) positions while Cu^{II} partially fills the (*c*) positions. Presumably the empirical composition of umangite, Cu_3Se_2, which is physically similar to rickardite but not isostructural, similarly represents $Cu_2Se \cdot CuSe$. These compounds recall the defective sulphide, digenite ("cubic chalcocite" or "blue chalcocite") with the cell formula $Cu_{8-x}S_4$. Typical examples closely conform to $x=1$, giving Cu_7S_4 or $3Cu_2S \cdot CuS$, representing a sulphide of copper of two kinds, as originally recognized by Breithaupt (1844, in Dana, 1944, p. 181) and expressed by his name digenite.

Finally, a word on the remarkable blue colour of rickardite and other copper ores is in order. Is this connected with defective structure, or with the presence of Cu in two valence states, or is it due essentially to Cu^{II}? The copper ore minerals whose body colours are blue in various degrees and the following:

Covellite, CuS	indigo
Germanite, $Cu_3(Fe, Ge)S_4$ or $3CuS \cdot (Fe, Ge)S$	purple
Rickardite, Cu_3Te_2 or $Cu_2Te \cdot CuTe$	purple
Umangite, Cu_3Se_2 or $Cu_2Se \cdot CuSe$	purple
Digenite, Cu_7S_4 or $3Cu_2S \cdot CuS$	blue

From these examples it would appear that the blue colour is due to copper atoms in the divalent state. The compound $Na_{1-x}WO_3$ affords an analogous example of blue colour associated with valence greater than normal (Hägg, 1935). As the composition of this substance varies from $x=0$ to $x=\frac{2}{3}$ an increasing proportion of W ions are raised in valence from W^{+5} to W^{+6} and the colour changes progressively from yellow, through red, to blue.

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