BRIEF COMMUNICATION

Low-Temperature Copper Ordering in the Layered Thiophosphate CuVP$_2$S$_6$: A Time-of-Flight Neutron Powder Diffraction Study

G. BURR

Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604

E. DURAND, M. EVAIN, AND R. BREC

Laboratoire de Chimie des Solides, I.M.N., 2 rue de la Houssiniere, 44072 Nantes Cedex 03, France

CuVP$_2$S$_6$ at room temperature is a layered structure with a statistical distribution of copper cations, Cu^I, on three different kinds of sites: triangular, tetrahedral, and octahedral. Upon cooling to 20 K, an ordering of the copper has been observed, whereas the low-temperature structure frame remains the same. The tetrahedral and octahedral sites are emptied, with the copper ions located entirely within the sulfur triangles at the edge of the structure slabs. The characteristics of the CuS$_3$ groups are the same as those of the least filled room-temperature sites. © 1993 Academic Press, Inc.

Introduction

In many compounds containing so-called d^{10} closed shell cations, a statistical distribution of those cations on several sites is frequently observed at room temperature. Cu^I and Ag^I, for instance, are found in different coordination sites in the same phase, leading to a split model description of the material in a classical structure determination. Those d^{10} cations also generally exhibit large calculated thermal parameters, suggesting either a complex static disorder, a dynamic disorder, or a strong asymmetric local movement.

A rather large number of phases in the $M^I M'^{III} P_2 X_6$ (M is Ag or Cu; M' is Cr, V, Sc, or In; and X is S or Se)(*1–7*) layered compound family are known to present the above structural features. Temperature and bond ionicity are two factors that act upon the occupancy ratio of the copper or silver sites. No structural determination of low-temperature polymorphs has ever been undertaken in the two-dimensional $M^I M'^{III} P_2 X_6$ series to study the Cu^I or Ag^I diffusion behavior. With three different copper site occupancies, it has been thought worthwhile to study CuVP$_2$S$_6$ at low temperature to determine possible ordering of copper between these sites.

The structure of room-temperature CuVP$_2$S$_6$ is based on a sulfur stacking of the $(ABC)_n$ type. One of the two intersulfur sheets is empty while the other one is ordered at the octahedral sites by cations which present a triangular arrangement, as shown
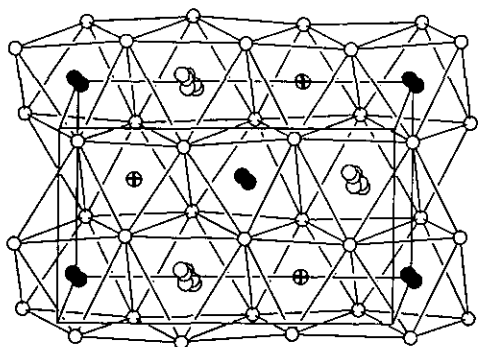
FIG. 1. Triangular cationic arrangement in the two-dimensional sheet (*ab* plane) of the room-temperature $CuVP_2S_6$ phase (black circles represent P, crossed circles represent V, large opened circles represent Cu, small opened circles represent S).

in Fig. 1. The vanadium cations occupy the centers of their own octahedra. The phosphorus atoms are found as P_2 pairs within their octahedra, but each phosphorus is in a tetrahedral environment (three sulfurs and one phosphorus). Within the remaining octahedra, the situation is more complex as shown by the distribution represented in Fig. 2 (7). Most of the copper is found at the
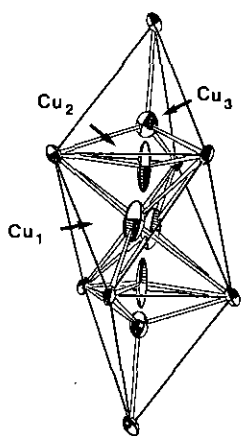

FIG. 2. View of the room-temperature copper distribution over the three different sites (triangular, tetrahedral, and octahedral) in and around a copper S_6 octahedron site.

van der Waals edge, next to the center of the trigonal sulfur windows of the S_6 octahedral(Cu2) and near the octahedral centers (Cu1 with two equivalent positions). The final copper site is located outside the M^1 octahedra, in the van der Waals gap itself and nearly on the Cu1–Cu2 axis. Cu3 is the smallest contribution (14%) to the copper total, but with a well defined position and with a small equivalent thermal factor (2.3 $\AA^2$ as compared to 4.6 and 4.5 $\AA^2$ for Cu1 and Cu2, with contributions of 30 and 56%, respectively).

A very low temperature (20 K) was chosen to study $CuVP_2S_6$ in order to obtain the highest possible ordering. The new copper arrangement observed by Rietveld refinement of time-of-flight neutron powder diffraction data is described in this article.

Experimental

Synthesis

The phase under study was prepared according to the conditions previously described (7). As mentioned, the materials also contained a small amount of Cu_3PS_4 as an impurity. Since this is quite detectable in the X-ray diffraction patterns, this means that the sample has several percent of the impurity. From the room-temperature X-ray data, the cell parameters of the majority phase were refined to check their agreement with the published values.

Neutron Powder Data

Time-of-flight (TOF) neutron diffraction data was collected on the High Intensity Powder Diffractometer (HIPD) at the Manual J. Lujan Neutron Scattering Center at Los Alamos National Laboratory. One gram of $CuVP_2S_6$ was loaded and sealed in a vanadium sample container in a helium-filled dry box. The sample and container were placed on HIPD and the sample compartment was evacuated, cooled, and main-

Space group: $C2$

Cell parameters: $a = 5.955(2)$ Å, $b = 10.321(3)$ Å,
$c = 6.699(2)$ Å and $\beta = 107.46°$ (1).

Detector bank (degrees): 153

Data range (msec): 3.785–24.000

Data range (Å): 0.75–3.80

Number of contributing reflections: Total = 1031
(Phase 1 = 581, phase 2 = 450)

Number of degrees of freedom: 3717

Number of variables: 48

R_{wp}: 0.0227, R_p: 0.0156, R_{expd}: 0.0131

tained at 20 K during the data collection. The sample was allowed to equilibrate at 20 K for several hours, then the data was collected for 8 hr.

The neutron powder diffraction data was analyzed by the Rietveld method (8) using the Generalized Crystal Structure Analysis System for TOF data (9, 10) (see Table I).

Structure Refinement

Initial positions for the vanadium, phosphorus, and sulfur were obtained from the previous single-crystal X-ray diffraction study (7). The copper position was located from a difference Fourier map. The data from the −153° bank of detectors was selected for refinement. A range of 0.75–3.80 Å was used from that bank. Atom positions, isotropic temperature factors, absorption, preferred orientation, lattice parameters, and profile coefficients were refined for CuVP₂S₆. For the impurity phase, Cu₃PS₄, absorption, preferred orientation, lattice parameters, and profile coefficients were refined. The atom positions were held at the position determined by the previous room temperature study. The background for the data set was fit with a refineable 12-term cosine Fourier series.

Results and Discussion

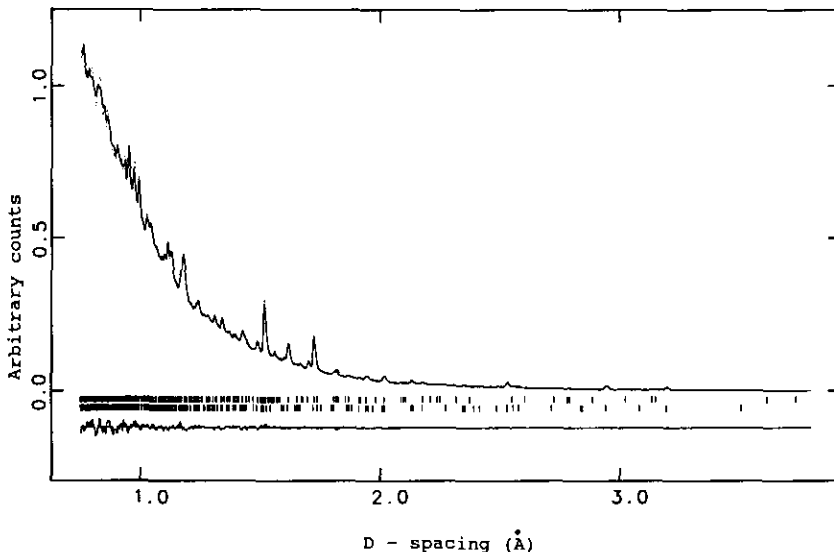The refinements were carried out in the $C2$ space group using all the atom positions

FIG. 3. Neutron counts per microsecond vs d-spacing of CuVP₂S₆ at 20 K over the range 0.75–3.80 Å. The measured data points are denoted by dots; the Rietveld profile is the solid line fitting the observations, and the difference (residual) is shown below the pattern. The tic marks represent the calculated d-spacing.
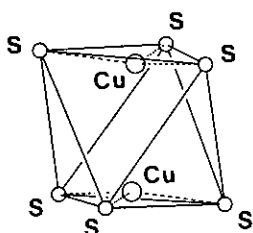
FIG. 4. Arrangement of copper in 20 K $CuVP_2S_6$. The copper Cu^I ions are located statistically on the opposite triangle faces of the sulfur octahedra within the structure slab.

from the room-temperature study except the copper cations. A difference Fourier map placed the copper ions essentially at the sulfur triangles of the octahedra, i.e., around the ambient temperature triangular positions, Cu2 and Cu3. With no copper at the octahedra center, the refinement was resumed with the two positions from the single-crystal structure determination. This refinement yielded unsatisfactory results with, in particular, negative isotropic thermal factors for one of the copper sites. In addition, the two copper positions were found exactly on each side of the S_3 triangles. A refinement with one single position in the middle of the S_3 groups led to a positive U_{iso} value, while the occupancy ratio set at 0.47(1), in good agreement with the analytical value of 0.5 for the chemical for-

mula. The last refinement cycle was completed with the theoretical occupancy leading to a reliability factor if 1.55 (wR = 2.26). The final difference plot for the neutron powder diffraction Rietveld refinement for the 20 K data is shown in Fig. 3. With a statistical distribution of copper in the triangular sites, it would be possible that one was dealing with an undetected and more ordered structure, with full occupancy of one site out of the two. In this hypothesis, one would observe the occurrence of a primitive cell. A superstructure should easily have been observed, since copper presents, by far, the higher diffusion coefficient in the structure. A very careful study of the pattern background did not reveal any extra weak peaks, ruling out, at least from powder data observation, the occurrence of further ordering among copper sites. Figure 4 shows the ordering of copper within the octahedral sulfur sites.

The final refined results yielded 92.5% $CuVP_2S_6$ and 7.5% Cu_3PS_4. The cell refinement gave the following values:
a = 5.955(2)Å, b = 10.321(3), c = 6.699(2), and β = 107.46(1)° for $CuVP_2S_6$. According to literature (11), the b/a ratio of exactly 1.732 indicates no distortion in the sulfur atom planes, whereas the $cos^{-1}(a/3c)$ value of 107.24° shows, compared to the observed β value of 107.46°, a meaningful departure from the ideal ABC stacking.

TABLE II

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z	U_{iso} (Å^2) × 100	t^a
V	0	0.33 (1)	0	2.0	
P	0.932 (1)	0	0.8234 (9)	1.7 (1)	
S1	0.724 (2)	0.676 (1)	0.244 (1)	0.4 (2)	
S2	0.270 (2)	0.839 (2)	0.255 (2)	2.9 (3)	
S3	0.747 (2)	0.488 (2)	0.756 (2)	4.1 (4)	
Cu	0.065 (2)	0.665 (1)	0.212 (1)	4.05 (2)	0.5

Note. The U_{iso} factor of vanadium has been set at 2.0 Å^2 and was not refined.

^{a} Multiplicity times occupancy ratio.

BRIEF COMMUNICATION

TABLE III

MAIN INTERATOMIC ANGLES (DEG) AND DISTANCES (Å) in $CuVP_2S_6$

P–S1	2.029 (13)	S1–V–S1	97. (6)
P–S2	2.023 (19)	S1–V–S2 ($\times 2$)	82.5 (19)
P–S3	2.059 (17)	S1–V–S2 ($\times 2$)	101.0 (27)
		S1–V–S3 ($\times 2$)	83.2 (5)
P–P	2.258 (13)	S2–V–S3 ($\times 2$)	94.2 (22)
		S2–V–S3 ($\times 2$)	82.3 (22)
V–S1	2.37 (10)	S3–V–S3 ($\times 2$)	97. (5)
V–S2	2.496 (14)		
V–S3	2.49 (10)	S1–Cu–S2	118.0 (9)
		S1–Cu–S3	121.9 (9)
Cu–S1	2.106 (16)	S2–Cu–S3	116.8 (7)
Cu–S2	2.142 (22)		
Cu–S3	2.120 (22)		

Tables II and III list the atomic positions and thermal parameters with their estimated standard deviations and the main interatomic angles and distances in $CuVP_2S_6$, respectively.

The first observation to be done is that all distances and angles compare well with those of the room-temperature (RT) data. For instance, the average V–S and P–S distances are equal to 2.467 Å (RT) and 2.452 Å (20 K) for the former and 2.028 Å (RT) and 2.039 Å (20 K) for the latter. Some increase is to be pointed out for the 20 K P–P distance(2.258 Å compared to 2.168 Å), the origin of which is unexplained. On the other hand, the characteristics of the triangular copper atom are nearly identical for both data sets(mean d_{Cu-S} are 2.128 and 2.122 Å and mean S–Cu–S angles of 118.8° and 118.9° for RT and 20-K samples, respectively). This indicates that the room-temperature triangular site is identical to what it is at lower temperature, that is, for the one which is stabilized upon cooling.

This situation of a single triangular site for copper is to be compared to that in the parent phase $Ag_2MnP_2S_6$, in which Ag^I is in that type of site already at room temperature (12), as shown by an anharmonic refinement study as a function of temperature. Now that copper ordering at 20 K has been found in this study, the same type of anharmonic refinement

study is now underway on $CuVP_2S_6$ to determine the nature of the Cu^I distribution, i.e., static or dynamic.

Acknowledgments

References

1. A. LEBLANC AND J. ROUXEL, C. R. Acad. Sci. Paris, Ser. C 291 (12), 263 (1980)
2. P. COLUMBET, A. LEBLANC, M. DANOT, AND J. ROUXEL, J. Solid State Chem. 41, 174 (1982).
3. P. COLUMBET, A. LEBLANC, M. DANOT, AND J. ROUXEL, J. Nouv. Chim. 7, 333 (1983).
4. S. LEE, P. COLUMBET, G. OUVRARD, M. DANOT, AND J. ROUXEL. Mater. Res. Bull. 21, 917 (1986).
5. G. OUVRARD AND R. BREC, Mater. Res. Bull. 23, 1191 (1988).
6. Z. QUILI, A. LEBRANC, AND P. COLUMBET. J. Solid State Chem. 66, 86 (1987).
7. E. DURAND, G. OUVRARD, M. EVAIN, AND R. BREC, Inorg. Chem. 29, 4916 (1990).
8. H. M. RIETVELD, J. Appl. Crystallogr. 2, 65 (1965).
9. A. C. LARSON AND R. B. VON DREELE, "Generalized Crystal Structure Analysis System," LAUR 86-748, Los Alamos National Laboratory, New Mexico (1986).
10. R. B. VON DREELE, J. D. JORGENSEN AND C. B. WINDSOR, J. Appl. Crystallogr. 15, 581 (1982).
11. G. OUVRARD AND R. BREC, Eur. J. Solid State Inorg. Chem. 27, 477 (1990).
12. A. VAN DER LEE, F. BOUCHER, M. EVAIN, AND R. BREC, Z. Für Krist. 203, 247–264 (1993).