

## Synthesis of Paramelaconite: $\text{Cu}_4\text{O}_3$

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DEDICATED TO THE MEMORY OF ALEXANDER F. WELLS

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Evidence for the natural occurrence and synthetic preparation of copper oxides other than  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  is reviewed. The unequivocal synthesis of  $\text{Cu}_4\text{O}_3$  (paramelaconite) is reported for the first time. It is achieved by extraction of copper or its oxides with concentrated aqueous ammonia in a Soxhlet apparatus. Quantitative X-ray diffraction analysis of one preparation showed that it consisted of 35%  $\text{Cu}_4\text{O}_3$ , 27%  $\text{Cu}_2\text{O}$ , and 38%  $\text{CuO}$  for a gross composition  $\text{CuO}_{0.77}$ . © 1996 Academic Press, Inc.

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### INTRODUCTION

Paramelaconite, subsequently shown to be a binary copper oxide with ideal composition  $\text{Cu}_4\text{O}_3$ , was discovered as a new mineral in the famous Copper Queen mine located at Bisbee, Arizona during the late 1870s. The composition and crystal class were first determined by Koenig (1) who named it after *melaconite*, a term no longer used for the mineral  $\text{CuO}$ . An exquisite specimen described by Koenig is now at the Seaman Mineral Museum at Michigan Technological University (# DM 13396). At least two other specimens were found at that time. These were originally purchased by the well-known dealer, Dr. A. E. Foote, who sold them in turn to Clarence S. Bement who was in the process of assembling what became one of the world's great mineral collections (for a fascinating account of Bement and his collection, see reference (2)). In 1900 the financier J. Pierpont Morgan purchased the entire Bement collection of some 12,300 specimens and presented it to the American Museum of Natural History. One magnificent paramelaconite crystal (AMNH 4630), about the size of a small finger (7.5-cm long), remains in New York, and the other specimen is now at the Smithsonian Institution in Washington (originally AMNH 4629, now Smithsonian #112878).

The first X-ray study was that by Frondel (3) who published an indexed powder pattern and correctly identified the space group as  $I4_1/amd$ . Frondel gave the composition as  $\text{CuO}_{0.88}$ , i.e., intermediate between  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  (=  $\text{CuO}_{0.5}$ ) and thus presumably containing  $\text{Cu(I)}$  and

$\text{Cu(II)}$ . A subsequent X-ray diffraction study by O'Keeffe and Bovin (4) on a chip of the Smithsonian crystal established the composition as  $\text{Cu}_4\text{O}_3$  and a structure was reported that showed clearly that the material should be written  $\text{Cu(I)}_2\text{Cu(II)}_2\text{O}_3$ . Those authors concluded that the reported composition (richer in O) was due to  $\text{CuO}$ , which also appeared in the powder diffraction pattern, and was present as inclusions and/or produced by oxidation during grinding. Partly because of a typographic error in this paper, and partly because of the common mistake of using the wrong origin for  $I4_1/amd$ , the structure has been on occasion misunderstood or misreported. In particular, the ICDD (formerly JCPDS) data base originally contained card number 3-879 with Frondel's (3) original data; however, this was superseded by card number 33-480 which contains a *calculated* powder diffraction pattern that is incorrect (see also below).<sup>1</sup> *Experimental* powder patterns (such as those presented in references (3, 4)) are bedeviled by the presence of overlaps with lines from  $\text{CuO}$ . For these reasons we give calculated powder diffraction patterns in Table 1.

At the same time as the report of O'Keeffe and Bovin (4), a structure for a specimen "obtained by courtesy of Professor Clifford Frondel" was reported by Datta and Jeffery (5) but those authors assumed that Frondel's analysis applied to a homogeneous crystal which they formulated as  $\text{Cu}_{12}^{2+}\text{Cu}_4^+\text{O}_{14}$ . Their structure had copper on two 8-fold positions so at least one of these has the unlikely partial occupancy of  $\text{Cu(I)}$  and  $\text{Cu(II)}$  and the structure also had an unphysical partial occupancy of oxygen sites. As the agreement index of O'Keeffe and Bovin ( $R = 3.5\%$ ) was substantially better than that of Datta and Jeffery ( $R = 8.3\%$ ), we believe that the former structure should be preferred.

<sup>1</sup> The coordinates given by O'Keeffe and Bovin (4) are correct but the coordinates of O(2) (0, 1/4, 3/8; etc.) were mislabeled 4a instead of the correct 4b. The origin used by these authors is at a center of symmetry on Cu(1) ("origin choice 2" in the *International Tables*). The JCPDS pattern 33-480 is calculated using coordinates appropriate for this origin but using a shifted origin ("origin choice 1" in the *International Tables*).

TABLE 1  
Calculated Powder Patterns for  $\text{Cu}_4\text{O}_3$ ,  $\text{CuO}$ , and  $\text{Cu}_2\text{O}^a$

$\text{Cu}_4\text{O}_3$			$\text{CuO}$			$\text{Cu}_2\text{O}$		
<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>	<i>d</i>	<i>I</i>	<i>hkl</i>
5.01	11	101						
3.16	7	112						
						3.012	41	110
2.91	26	200						
2.87	5	103						
			2.749	60	110			
			2.529	299	002			
			2.522	800	11 $\bar{1}$			
2.517	3	211						
2.507	1000	202						
						2.496	1000	111
2.470	163	004						
			2.321	1000	111			
			2.309	233	200			
						2.130	382	200
2.058	190	220						
2.042	3	213						
			1.960	17	46			
1.904	11	204						
			1.867	299	20 $\bar{2}$			
			1.776	12	112			
						1.739	11	211
1.725	2	312						
			1.710	119	020			
1.581	297	224						
			1.579	163	202			
			1.505	227	11 $\bar{3}$			
						1.506	359	220
1.455	108	400						
1.433	157	206						
			1.417	183	02 $\bar{2}$			
			1.409	177	31 $\bar{1}$			
			1.378	112	113			
			1.374	163	220			
1.301	2	420						
			1.303	91	311			
						1.284	330	311
			1.264	69	004			
1.258	193	422						
			1.261	80	22 $\bar{2}$			
1.254	71	404						
1.235	29	008						
						1.230	78	222

<sup>a</sup> No temperature factors have been included. Lines are reported for  $I/I_{\text{max}} \geq 0.001$  for  $\text{Cu}_4\text{O}_3$ , and for  $I/I_{\text{max}} \geq 0.01$  for  $\text{CuO}$  and  $\text{Cu}_2\text{O}$ . For  $\text{Cu}_4\text{O}_3$  we use  $a = 5.82$ ,  $c = 9.88$  Å.

The Smithsonian Institution has another specimen (#138844) of paramelaconite which may have been originally part of the Bisbee specimen (#112878) although the provenance is given as “from Jerome Arizona”.<sup>2</sup> X-Ray

<sup>2</sup> Possibly from the United Verde Mine. This location is about 400 km from Bisbee.

diffraction studies (6) confirmed that this material is predominantly paramelaconite. Other small specimens from Bisbee, thought to be part of the original find, are in private collections (R. Thomssen, private communication).

An identification (7) as paramelaconite of material from the Algomah mine, Michigan, and presently in the Seaman Museum is believed to be correct (8), although one museum specimen thought to be authentic paramelaconite (# AES 38) is rather small, and we found by X-ray diffraction that a fragment of a “crystal” from that specimen was polycrystalline  $\text{CuO}$ . In addition, numerous specimens labeled “paramelaconite” from that location and elsewhere have been separately investigated by us (BLC and MO’K, unpublished) and by R. S. Roth (private communication); the only copper-containing phase identified in these samples was tenorite ( $\text{CuO}$ ). Certainly most, if not all, authentic specimens extant came from the original find in the Copper Queen mine. Geologists, and others, would be interested to know the conditions under which such rare and beautiful crystals were formed.

$\text{Cu}_2\text{O}$  was one of the original “electronic materials” (e.g., once used on a large scale in rectifiers) and  $\text{CuO}$  has the remarkable property of a large but almost constant paramagnetic susceptibility at low temperatures (9). The discovery of the superconducting mixed-valence copper oxides and the possible role of magnetic interactions facilitating the very high  $T_c$  has intensified the interest in the binary oxides. For example, the magnetic properties of  $\text{CuO}$  are currently the subject of intense theoretical and experimental study (for representative papers which give references to other work see (10)). For such reasons it would be interesting to have available synthetic routes to pure specimens of  $\text{Cu}_4\text{O}_3$  for studies of its physical properties.

In this paper we discuss next some reports of copper oxides other than  $\text{Cu}_4\text{O}_3$  and the well-established phases  $\text{Cu}_2\text{O}$  (cuprite) and  $\text{CuO}$  (tenorite). We then mention some earlier work on the synthesis of paramelaconite, and finally report the serendipitous discovery (by PEDM) of a synthetic route to crystalline  $\text{Cu}_4\text{O}_3$  and its subsequent elaboration by the ASU group. We dedicate the paper to the memory of A. F. Wells who perhaps loved the structures of Cu oxide minerals (e.g., (11)) more than all the other myriad structures of which he was master (12).

## OTHER COPPER OXIDES

The essential features of the Cu–O phase diagram at pressures less than 1 atm have long been established (13, 14) although we note that early phase diagrams showed that  $\text{Cu}_2\text{O}$  was unstable to disproportionation below about 650 K, and one still finds the statement that  $\text{CuO}$  “is the only thermodynamically stable phase” at low temperatures (15). Although  $\text{Cu}^+$  disproportionates to  $\text{Cu}^0 + \text{Cu}^{2+}$  in

aqueous solution, it is easy to show that anhydrous Cu<sub>2</sub>O is stable. Thus from standard thermodynamic tables (16) one finds that  $\Delta G^0$  for Cu<sub>2</sub>O<sub>(c)</sub> → CuO<sub>(c)</sub> + Cu<sub>(c)</sub> ranges from +15 kJmol<sup>-1</sup> at 0 K to +29 kJmol<sup>-1</sup> at 1000 K. Recent studies (17) of the Cu–O system at high oxygen activities revealed no new copper oxides.

Nevertheless, reports of copper oxides of compositions other than Cu<sub>2</sub>O, Cu<sub>4</sub>O<sub>3</sub>, and CuO have appeared in the literature; these fall into one of two categories: (a) Cu-rich thin films with compositions such as Cu<sub>8</sub>O (18) and Cu<sub>64</sub>O (19) observed in an electron microscope, and (b) compositions such as Cu<sub>3</sub>O<sub>2</sub> claimed from gravimetric and other studies of oxidized copper but for which no definitive structural data are available. We do not consider the compounds under (a) any further as they are essentially Cu metal with low (metastable) levels of interstitial oxygen, but Cu<sub>3</sub>O<sub>2</sub> deserves more consideration.

Cu<sub>3</sub>O<sub>2</sub> was first reported to form as an intermediate oxide in the low-temperature oxidation of copper by Czanderna and co-workers (20–22) and subsequently by others (23, 24); recent work (15) considered this phase to be established “unambiguously.” The material appears to be a metastable oxygen-rich extension of the cuprite phase field as its diffraction pattern is almost identical to that of cubic Cu<sub>2</sub>O, but with  $a = 4.31(1)$  Å (cf.  $a = 4.27$  Å for Cu<sub>2</sub>O), and Cu<sub>3</sub>O<sub>2</sub> and Cu<sub>2</sub>O have similar IR reflectance spectra. Magnetic evidence for metastable Cu<sub>2</sub>O<sub>1+x</sub> ( $x \approx 0.1$ ) produced by low-temperature oxidation of Cu<sub>2</sub>O was presented earlier by O’Keeffe and Stone (25) and we consider that “Cu<sub>3</sub>O<sub>2</sub>” is best considered as an extension of stoichiometric cuprite.

#### PREVIOUS ATTEMPTS TO PREPARE Cu<sub>4</sub>O<sub>3</sub>

Long and Petford-Long (26) showed that microscopic quantities of Cu<sub>4</sub>O<sub>3</sub> are produced on decomposition of CuO in the beam of an electron microscope, however, there is no obvious way to scale up this method to produce macroscopic samples suitable for physical properties measurement.

Unsuccessful synthesis are rarely reported, however, we know of several laboratories where concerted efforts were made to effect a synthesis (including the group of BLC at the University of Connecticut). Despite many man-years of effort, successful synthesis was not achieved. The symproportionation reaction  $2\text{CuO} + \text{Cu}_2\text{O} \rightarrow \text{Cu}_4\text{O}_3$  does not occur at normal pressure and temperature and, as the volume change is  $\Delta V = +6.6 \times 10^{-6}$  m<sup>3</sup>mol<sup>-1</sup> for the reaction as written, the reaction is even less likely to occur at high pressure. Other experiments focused on carefully-controlled reduction of CuO by reducing gases and decomposition in a vacuum. In yet other experiments, synthesis was attempted by controlled oxidation of Cu<sub>2</sub>O; again without success.

TABLE 2  
Refined (or Reported) Unit Cell Parameters Calculated from the Published Powder Data for Paramelaconite and for Cu<sub>4</sub>O<sub>3</sub>, e.s.d. in Parentheses for Refined Data

$a$ (Å)	$c$ (Å)	Author
5.817(2)	9.861(5)	Frondel (3)
5.823(3)	9.903(7)	O’Keeffe and Bovin (4)
5.817	9.893	Datta and Jeffery (5)
5.817(2)	9.894(3)	Chamberland (6)
5.813(1)	9.874(1)	This work (Cu <sub>4</sub> O <sub>3</sub> from Cu wool)
5.818(2)	9.894(3)	This work (Cu <sub>4</sub> O <sub>3</sub> from CuO, wire form)

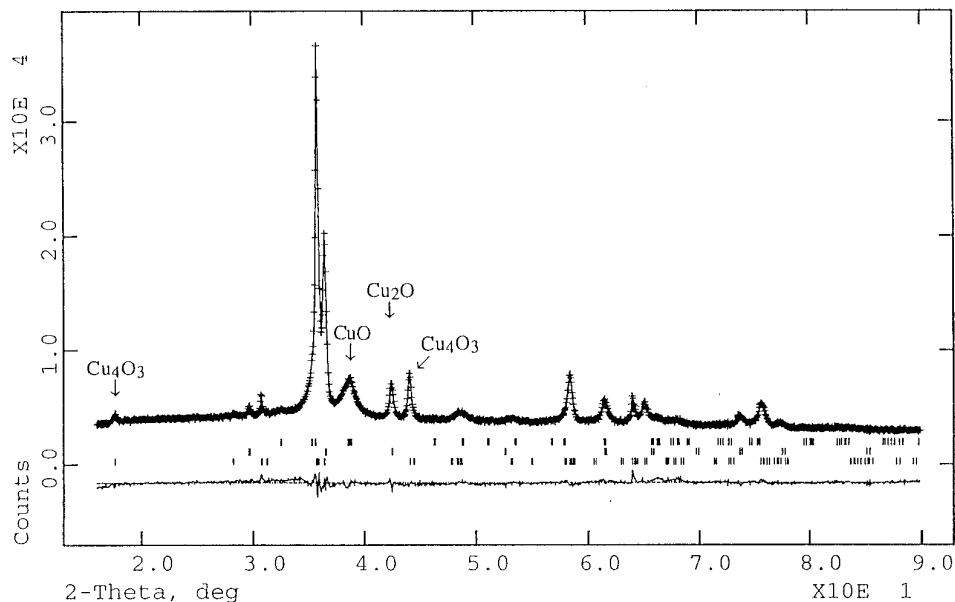
Numerous experiments were performed over several years at NIST (then NBS) in which copper oxides were produced from high-temperature (up to 250°C) aqueous solutions. The only materials obtained were CuO and Cu<sub>2</sub>O (27).

Oxidation of copper or copper-containing alloys does not yield Cu<sub>4</sub>O<sub>3</sub> although there have been reports to the contrary. A report (28) on the corrosion of copper exposed to the atmosphere in the Arabian Gulf claims that paramelaconite is formed after several years of exposure. However, the only evidence for paramelaconite formation was one very weak X-ray diffraction peak at approximately 3.2 Å. This line is only a very weak line in the powder pattern of paramelaconite (see  $d = 3.16$  in Table 1) but it is reported as the strongest line in the erroneous ICCD file 33-480 mentioned above; it is likely that the author was led astray by the incorrect calculated powder pattern, and examination of the published pattern of the corrosion product shows no evidence for Cu<sub>4</sub>O<sub>3</sub>. Another report (29) of the possible production of paramelaconite (which was formulated as Cu<sub>2</sub>O · 6 CuO) on the oxidation of copper alloys (brasses) was based on what appears to us to be rather skimpy evidence (a single X-ray diffraction line at  $d = 2.04$  Å).

#### SUCCESSFUL SYNTHESSES

The basis of the successful method of preparing Cu<sub>4</sub>O<sub>3</sub> is the extraction/leaching of a source of copper in a Soxhlet extractor with concentrated aqueous ammonia contained in a round-bottomed flask that serves as reservoir. The original experiments (carried out by PEDM more than 20 years ago) involved extraction of Cu from copper wastes, but we have since explored the use of copper metal (as “wool”), Cu<sub>2</sub>O and CuO.<sup>3</sup> The initial reaction produces a deep blue cupric ammonium complex which is converted

<sup>3</sup> The ammonia leaching process for recovery of copper appears to have been introduced in 1912 by C. H. Benedict at the Calumet & Hecla mine in Michigan (30).



**FIG. 1.** X-Ray diffraction profile fit for  $\text{Cu}_4\text{O}_3$  (bottom reflection markers),  $\text{Cu}_2\text{O}$  (middle), and  $\text{CuO}$  (top). The data are shown as +. The solid line is the calculated profile and the difference curve is shown below on the same scale. Both reflections resulting from  $\text{Cu}K_{\alpha 1}$  and  $K_{\alpha 2}$  are shown. Note the signature peaks of the three phases labeled accordingly.

to a black oxide residue on the walls of the refluxing vessel where it is returned by siphon action. The conditions for optimum yield are yet to be established, but some empirical observations follow. With pure  $\text{CuO}$  the yields are very small,  $\text{CuO}$ – $\text{Cu}_2\text{O}$  work rather well, and the best yields are obtained from  $\text{Cu}$  or  $\text{Cu}_2\text{O}$  in the presence of air. When metallic copper is used as the starting material, and oxygen is excluded (by flushing with argon), the yield of oxide is very small. The black deposit forms on the walls of the refluxing vessel, and if boiling is too vigorous or the solution is stirred, the yield is also greatly diminished. The optimum yield appears to result after 2 to 5 days, the synthesis being achieved at temperatures around  $100^\circ\text{C}$ . A prolonged run of several weeks resulted in a suspension of a white amorphous material that has not been analyzed chemically, but which might be expected to contain ions such as ammonium and (bi)carbonate.

X-ray analyses of the black deposits show that they consist solely of copper oxides, and the diffraction peaks at  $d = 5.01$  and  $2.06 \text{ \AA}$  (see Table 1) are the signature of  $\text{Cu}_4\text{O}_3$ . Likewise, the presence of  $\text{Cu}_2\text{O}$  is readily recognized by a peak at  $d = 2.13 \text{ \AA}$ .  $\text{CuO}$  is indicated by the strong peaks at  $d = 2.32$  and  $2.31 \text{ \AA}$ ; in our preparations these are rather broad. Because of overlap of strong peaks, quantitative analysis of the mixtures requires careful analysis of the X-ray data. In a typical analysis we obtained two sets of data, each being the sum of ten individual scans on a Rigaku D/max-IIB powder diffractometer. We then refined the data using the program GSAS, a Rietfeld re-

finement code developed by Larson and Von Dreele (31). Parameters refined included unit cell parameters for  $\text{CuO}$ ,  $\text{Cu}_2\text{O}$ , and  $\text{Cu}_4\text{O}_3$ , the O parameter in  $\text{Cu}_4\text{O}_3$ , isotropic thermal parameters for all atoms, and background fitting parameters. For the fit shown in Fig. 1,  $\chi^2 = 4.6$ ,  $R_p = 3.17\%$ , and  $R_{wp} = 2.43\%$  for the 27 parameters. The refined structure of  $\text{Cu}_4\text{O}_3$  is in good agreement with that reported earlier (4) although the unit cell parameters determined are slightly smaller (Table 2). The distribution of Cu in the three phases on an atomic basis was found to be 35%  $\text{Cu}_4\text{O}_3$ , 27%  $\text{Cu}_2\text{O}$ , and 38%  $\text{CuO}$  for a gross composition  $\text{CuO}_{0.77}$ . This composition is very close to that expected ( $\text{CuO}_{0.75}$ ) for paramelaconite suggesting that the composition may be the primary product nucleating from solution, and that the other oxides are secondary products of disproportionation (notice that the  $\text{CuO}$  peaks are broad). Paramelaconite is found in all our preparations. A TGA experiment on the crude product (containing approximately 40%  $\text{Cu}_4\text{O}_3$ ) in an helium atmosphere showed a slight weight loss to approximately  $110^\circ\text{C}$  (possibly absorbed water), then a larger weight loss with the eventual formation of  $\text{Cu}_2\text{O}$  at  $300^\circ\text{C}$ .

Detailed speculation on the mechanism of reaction is premature, but the following observations are relevant. We find that  $\text{Cu}$  and  $\text{Cu}_2\text{O}$  are readily soluble in concentrated ammonia solutions in the presence of air, but the metal does not dissolve if air is excluded (i.e., under an argon atmosphere). Pure  $\text{CuO}$  is less readily soluble, but material such as  $\text{CuO}$  wire (which invariably contains  $\text{Cu}_2\text{O}$ ) will

eventually dissolve in an aqueous ammonia solution. It is tempting to suppose that the solution species involves both Cu(I) and Cu(II). It is also possible that Cu<sub>4</sub>O<sub>3</sub> is unstable above 100°C which would go far in explaining its difficulty of preparation by ceramic methods.

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### REFERENCES

1. G. A. Koenig, *Proc. Acad. Nat. Sci. Philadelphia* 248 (1891).
2. J. J. Peters and C. L. Pearson, *Mineral Rec.* **21**, 47 (1990).
3. C. Frondel, *Am. Mineral.* **26**, 657 (1941).
4. M. O'Keeffe and J.-O. Bovin, *Am. Mineral.* **63**, 180 (1978).
5. N. Datta and J. W. Jeffery, *Acta Crystallogr. Sect. B* **34**, 22 (1978).
6. B. L. Chamberland, unpublished results.
7. S. A. Williams, *Am. Mineral.* **47**, 778 (1962).
8. S. J. Dyl II, personal communication.
9. M. O'Keeffe and F. S. Stone, *J. Phys. Chem. Solids* **23**, 161 (1962).
10. U. Köbler and T. Chattopadhyay, *J. Phys. B. Condens. Matter* **82**, 383 (1991); M. Ain, A. Menellet, B. M. Wanklyn and E. F. Bertaut, *J. Phys. Condens. Matter* **4**, 5327 (1992); S. B. Ota and E. Gmelin, *Phys. Rev. B* **46**, 11632 (1992).
11. A. F. Wells, *Acta Crystallogr.* **2**, 175 (1949).
12. A. F. Wells, "Structural Inorganic Chemistry," 1st–5th ed. Oxford Univ. Press, London, 1945–1984.
13. F. H. Smyth and H. S. Roberts, *J. Am. Chem. Soc.* **42**, 2582 (1920).
14. B. Reuter and X. Schröder, *Z. Anorg. Allg. Chem.* **277**, 146 (1954).
15. M. Lenglet, K. Kartouni, J. Machefer, J. M. Claude, P. Steinmetz, E. Beauprez, J. Heinrich, and N. Celati, *Mater. Res. Bull.* **30**, 393 (1995).
16. M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald, and A. N. Syverud, "JANAF Thermochemical Tables," 3rd ed. *J. Phys. Chem. Ref. Data* 14, Supplement 1 (1985).
17. G. A. Slack, G. Demazeau, T. Plant, and L. Raberdel, *Phys. Rev. Sect. B* **47**, 12019 (1993).
18. R. Guan, H. Hashimoto, and K. H. Kuo, *Acta Crystallogr. Sect. B* **40**, 560 (1984).
19. R. Guan, H. Hashimoto, and K. H. Kuo, *Acta Crystallogr. Sect. B* **41**, 219 (1985).
20. H. Wieder and A. W. Czanderna, *J. Phys. Chem.* **66**, 816 (1962).
21. A. W. Czanderna and H. Wieder, *J. Chem. Phys.* **39**, 489 (1963).
22. E. G. Clark and A. W. Czanderna, *Surf. Sci.* **49**, 529 (1975).
23. H. Neumeister and W. Jaenicke, *Z. Phys. Chem. N. F.* **108**, 217 (1978).
24. B. Lefez, K. Kartouni, M. Lenglet, D. Rönnow, and C. G. Ribbing, *Surf. Interface Anal.* **22**, 451 (1994).
25. M. O'Keeffe and F. S. Stone, *Proc. R. Soc. London Ser. A* **267**, 501 (1962).
26. N. J. Long and A. K. Petford-Long, *Ultramicroscopy*, **20**, 151 (1986).
27. R. S. Roth, personal communication.
28. E. A. Taqi, *Br. Corros. J.* **29**, 75 (1994).
29. G. P. Ponzano, O. Barbangelo, and P. L. Bonora, *Ann. Chim. (Rome)* **65**, 561 (1975).
30. M. L. Wilson and S. J. Dyl II, *Mineral. Rec.* **23**(2), 7 (1992).
31. A. C. Larson and R. B. Von Dreele, "Generalized Structure Analysis System." LANSCE, MS-H805, Manuel Lujan Neutron Scattering Center, Los Alamos, NM 87545, 1989.