STRUCTURAL DISORDER IN LINDSTRÖMITE: A BISMUTHINITE – AIKINITE DERIVATIVE

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ABSTRACT

High-resolution electron microscopy is used to examine the nature and extent of structural disorder in lindströmite, $Cu_3Pb_3Bi_7S_{15}$, a member of the bismuthinite – aikinite series. Well-ordered regions of lindströmite were found to be intergrown with lamellae of krupkaite, $CuPbBi_3S_6$. Aikinite lamellae were also observed within extensive regions of krupkaite, and homogeneous regions of krupkaite and hammarite were also detected. An understanding of the mechanism of compositional variation in the end-member phases bismuthinite and aikinite will require further study.

Keywords: high-resolution electron microscopy, lindströmite, aikinite, krupkaite, hammarite, bismuthinite series, compositional fields, structural disorder, type specimen.

SOMMAIRE

On a étudié la nature et la portée du désordre structural dans la lindströmite $Cu_3Pb_3Bi_7S_{15}$, membre de la série bismuthinite – aikinite, par microscopie électronique à haute résolution. Des régions bien ordonnées de lindströmite sont juxtaposées à des lamelles de krupkaïte $CuPbBi_3S_6$. On voit aussi des lamelles d'aikinite dans des domaines de krupkaïte, et des régions homogènes de krupkaïte et de hammarite. Une connaissance du mécanisme de variation de la composition des pôles bismuthinite et aikinite requiert une étude plus approfondie.

(Traduit par la Rédaction)

Mots-clés: microscopie électronique à haute résolution, lindströmite, aikinite, krupkaïte, hammarite, série de la bismuthinite, champs de composition, désordre structural, échantillon type.

INTRODUCTION

The chemical and structural nature of the bismuthinite – aikinite series has been extensively studied (Makovicky 1981). Six mineral phases that are chemically intermediate between bismuthinite Bi_2S_3 and the fully stuffed aikinite $CuPbBiS_3$ have been identified (Table 1). The bismuthinite structure is the archetype for the group, the structure of the other minerals being derived by ordered substitution of cations, insertion of Cu and supercell ordering. It can be viewed as composed of quadruple Bi_4S_6 chains in which half the bismuth is in three-fold co-ordination, and the other half is five-co-ordinate,

forming Bi_4S_6 ribbons (Kupčík & Veselá-Nováková 1970) (Fig. 1a). But the structure can also be readily derived from the NaCl type by shear of the $\{113\}_{f.c.c.}$ layers and periodic twinning (Hyde *et al.* 1979). In this structure, the co-ordination polyhedra of bismuth are best visualized as capped trigonal prisms, of which there are two crystallographically distinct sets (Fig. 1b).

Aikinite is derived from bismuthinite by replacing half of the Bi^{3+} by Pb^{2+} (+ interstitial Cu^+) in an ordered fashion (Ohmasa & Nowacki 1970, Kohatsu & Wuensch 1971). Compositionally, krupkaite $CuPbBi_3S_6$ lies midway between bismuthinite and aikinite: only one quarter of the Bi^{3+} are replaced by Pb^{2+}, and Cu^+ occupies only half the available tetrahedral sites. This substitution also occurs in an ordered fashion, and results in a non-centric structure rather than the centric structures of bismuthinite and aikinite (Mumme 1975). The structures of the other intermediate members are composed of ordered intergrowths of bismuthinite (*b*), krupkaite (*k*) and aikinite (*a*) ribbons.

Structurally, lindströmite $Cu_3Pb_3Bi_7S_{15}$ is the most complex intermediate member, being based on a ten-ribbon intergrowth $(2a + 8k)$. Its unit cell is *a* 56.11, *b* 11.57, *c* 4.00 Å; thus it is a $5a$ supercell of bismuthinite (Fig. 2). The structure was determined by Horiuchi & Wuensch (1977), but not without considerable difficulty. To refine the structure fully, they found it necessary to assume that the crystal studied contains 6.3 vol.% of exsolved krupkaite.

In contrast to the highly ordered intergrowth-structures reported for the intermediate phases, Harris & Chen (1976) reported extensive solid-solution fields for the end-members aikinite and krupkaite. The degree of chemical segregation required for the formation of the well-ordered intergrowth-structures of the intermediate phases seems at odds with the concept of large compositional fields due to solid solution in the end members. The compositional fields could well be due to the disordered intergrowth of end-member ribbons.

We undertook high-resolution electron-microscopy studies of lindströmite to confirm the structure and to determine the nature of the krupkaite exsolution assumed by Horiuchi & Wuensch (1977).

TABLE 1.   MINERALS IN THE BISMUTHINITE - AIKINITE SERIES

Mineral	Composition	a Å	b Å	c Å	Space Group	Structure	Reference
Bismuthinite	Bi_2S_3	11.23	11.27	3.91	Pbnm	b	Kupčík & Veselá-Nováková (1970)
Pekoite	$CuPbBi_{11}S_{18}$	33.50	11.32	3.99	$Pb2_1m$	4b + 2k	Mumme & Watts (1976)
Gladite	$CuPbBi_5S_9$	33.66	11.45	4.02	Pbnm	2b + 4k	Kohatsu & Wuensch (1976)
Krupkaite	$CuPbBi_3S_6$	11.15	11.51	4.01	$Pb2_1m$	k	Mumme (1975)
Lindstromite	$Cu_3Pb_3Bi_7S_{15}$	56.07	11.57	4.01	$Pb2_1m$	8k + 2a	Horiuchi & Wuensch (1977)
Hammarite	$Cu_2Pb_2Bi_4S_9$	33.45	11.58	4.01	Pbnm	4k + 2a	Horiuchi & Wuensch (1976)
Friedrichite	$Cu_5Pb_5Bi_7S_{18}$	33.84	11.65	4.01	$Pb2_1m$	2k + 4a	Chen et al. (1978)
Aikinite	$CuPbBiS_3$	11.32	11.64	4.04	Pbnm	a	Kohatsu & Wuensch (1971)
							Ohmasa & Nowacki (1970)

b = bismuthinite ribbons   k = krupkaite ribbons   a = aikinite ribbons

EXPERIMENTAL

Several small crystal fragments of lindströmite from the type specimen (RM24100) were obtained from Dr. Eric Welin, Naturhistoriska Riksmuseet, Stockholm. Crystals were ground under acetone in an agate mortar and dispersed on Cu grids coated with holey-carbon support films. The fragments were examined in a JEM 200CX electron microscope fitted with an ultrahigh-resolution top-entry goniometer ($\pm$ 10°), objective lens with C_s = 1.20 mm and a LaB_6 filament. Crystal fragments projecting over holes in the carbon film were tilted into the [001] zone. Lattice images, at 380,000× magnification, and electron-diffraction patterns were recorded using exposures of 2-4 s.

OBSERVATIONS

A series of [001]-zone electron-diffraction patterns was taken from various fragments of the specimen (Fig. 3). The range of diffraction patterns attests to the inhomogeneity of the type material: Figure 3a shows only the strong rectangular array of subcell reflections, which corresponds to the basic bismuthinite–krupkaite–aikinite cell ($\sim$11.2 × 11.6 Å). Figure 3b has the same set of subcell reflections plus additional weaker reflections (spacing $a*/5$) along $a*$, presumably due to the ordering of krupkaite and aikinite ribbons in the lindströmite structure. The superlattice reflections are somewhat streaked (cf. Fig. 3d), indicating the presence of some disorder. A highly ordered superstructure is, however, dominant. In crystal fragments where disorder (of krupkaite and aikinite ribbons) predominates, the supercell reflections are reduced to weak streaks along $a*$ (Fig. 3c). Regions of hammarite, with a $3a$ supercell, were found intergrown with krupkaite and lindströmite in the specimen (Fig. 3d). Note that the superlattice reflections are very sharp, indicating that the supercell is well ordered, a conclusion confirmed by the lattice images.

A lattice image of the well-ordered lindströmite crystal (corresponding to Fig. 3b) is shown in Figure 4a. Its $5a$ supercell dominates this low-magnification image, but the crystal also contains a 200-Å lamella of krupkaite on the right. Dark patches in the image are due to damage by the electron beam. Note that the image contains two types of ribbons that differ in contrast: the ordering of the ribbons is clearly visible. Figure 4b shows a disordered intergrowth of krupkaite and aikinite units, with some small regions of the lindströmite structure. Large regions of perfectly ordered lindströmite structure were not encountered in this study, although several regions of well-ordered hammarite were noted (Fig. 4c).

Interpretation of the images

The observation of well-ordered lindströmite regions interlaced with exsolution lamellae of krupkaite in the type material serves to confirm and clarify the findings of earlier workers. During their structure refinement, Horiuchi & Wuensch (1977) had to assume that their crystal of lindströmite contains 6.3% exsolved krupkaite. The electron micrographs demonstrate the validity of this assumption. Welin (1966) observed exsolution lamellae in the hand specimen, and demonstrated by electron-microprobe analysis that these lamellae represent a sulfosalt of the bismuthinite – aikinite group but of a slightly different composition. What Welin found were clearly exsolution lamellae of krupkaite in lindströmite. The lattice images show that these lamellae extend throughout much of the sample, albeit on a very fine scale (100–200 Å in some cases). The imaging studies also reveal that the type specimen consists of an intergrowth of lindströmite, krupkaite and hammarite.

More detailed structural and compositional interpretation of the lattice images is greatly hampered by the large thickness of the crystal fragments and the complex nature of the structure: image detail is highly sensitive to thickness, and to beam tilt and defocus of the objective lens. Given that the image
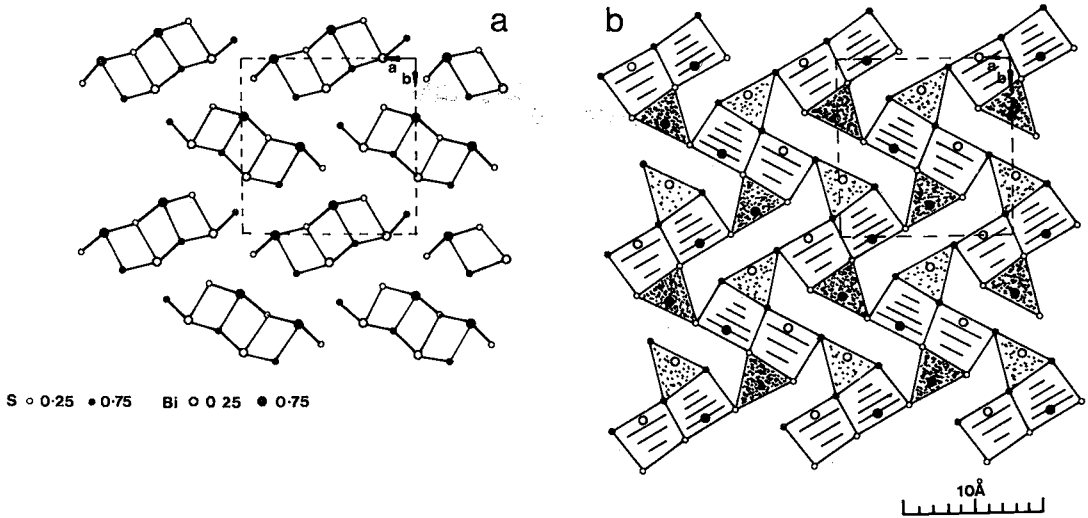
S ○ 0·25 ● 0·75   Bi ○ 0 25 ● 0·75

FIG. 1. Schematic diagrams of the structure of bismuthinite down [001]. (a) Bi_4S_6 chains in which half the number of bismuth atoms is three-co-ordinate and the other half is five-co-ordinate (Kupčík & Veselá-Nováková 1970). (b) Bismuth co-ordination polyhedra, two crystallographically distinct sets of capped trigonal prisms (Hyde *et al.* 1979) (the capping is not shown).
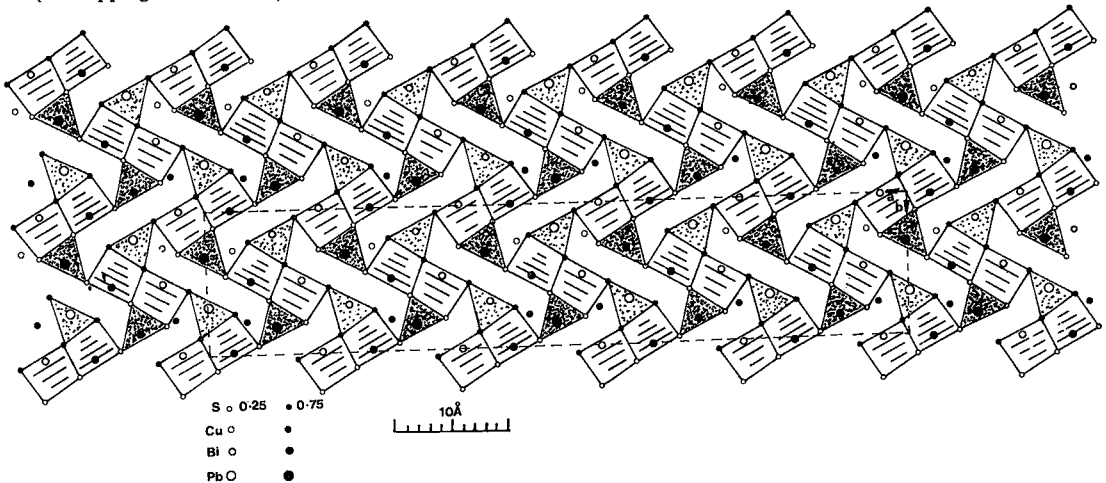

S ○ 0·25 ● 0·75
Cu ○ ●
Bi ○ ●
Pb ○ ●

FIG. 2. Schematic diagram of the structure of lindströmite, $Cu_3Pb_3Bi_7S_{15}$, down [001]. Structure is composed of an ordered intergrowth of 2 aikinite and 8 krupkaite ribbons. Copper atoms occupy tetrahedral sites.

in Figure 4a was recorded with the value of objective lens defocus near the Scherzer defocus (−800 Å), limited direct-image interpretation can be made by considering charge density alone. Image detail is dominated by two types of ribbons, the darker ribbons being in the minority. The lindströmite structure contains aikinite and krupkaite ribbons in the ratio 1:4; this is approximately the ratio of dark and light ribbons in the lattice images, suggesting that the dark strips are aikinite-type ribbons. Pb and Bi are indistinguishable, but the darker aikinite corresponds to the larger concentration of interstitial copper atoms [krupkaite: $Cu(PbBi_3)S_6$, aikinite: $Cu_2(Pb_2Bi_2)S_6$]. The effects of thickness on image

contrast can be seen in Figure 4b; the contrast between the two types of ribbons is reversed, so that here the light ribbons are aikinite.

Ranges in composition

The composition of lindströmite was established by Welin (1966) as $Cu_6Pb_6Bi_{14}S_{30}$ [= $Cu_4Pb_4Bi_{12}S_{24}$ + $Cu_2Pb_2Bi_2S_6$, *i.e.*, 4 krupkaite to 1 aikinite]; this was later confirmed by results of a crystal-structure analysis (Horiuchi & Wuensch 1977). The currently accepted formula differs slightly from the composition given in the original description by Johannson (1924), $CuPbBi_3S_6$, which is the currently accepted
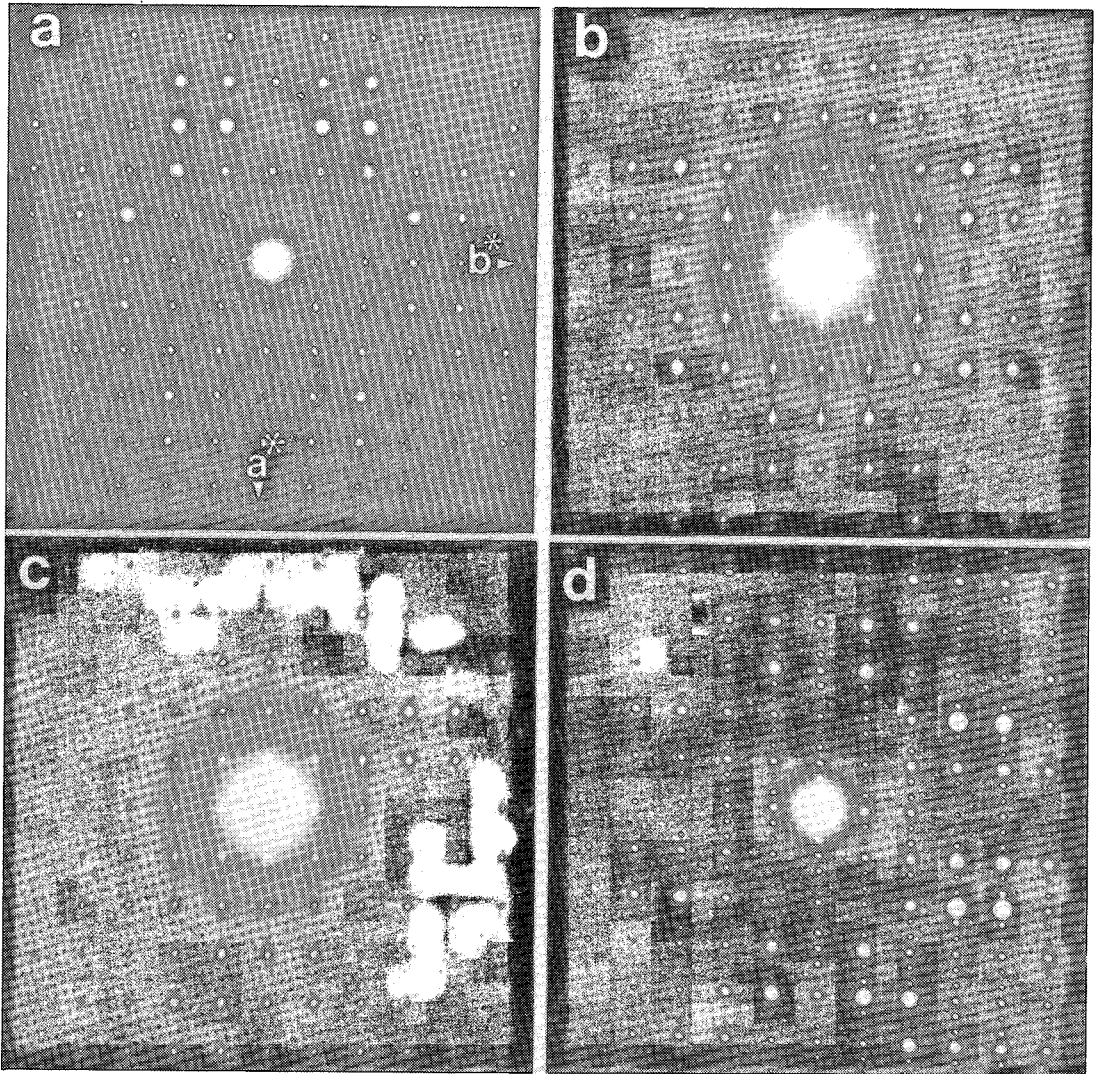
FIG. 3. Electron-diffraction patterns taken down the [001] axis (lindströmite setting). (a) Krupkaite. (b) Lindströmite (note the supercell reflections corresponding to a $5a$ supercell). (c) Disordered krupkaite – aikinite intergrowth (note streaking along a^*). (d) Hammarite (showing well-developed $3a$ supercell).

formula for krupkaite. The difference between the two compositions is small and most probably due to Johannson's chance selection of a portion of the type specimen in which krupkaite predominates. Large domains of pure krupkaite were found in the type material during this study (Fig. 5).

In addition to the fragments of lindströmite, hammarite and krupkaite found by electron microscopy, many regions of disorder were encountered. The disordered crystals fall into two broad categories: 1) lindströmite with krupkaite disorder, and 2) krupkaite with aikinite disorder. The widespread intergrowth of ribbons of aikinite and krupkaite within a matrix of krupkaite or lindströmite provides a ready mechanism for significant variation from the ideal composition. Extensive solid solution has been reported in natural materials for both aikinite, $Cu_{1-x}Pb_{1-x}BiS_{3-x}$ ($0 \leq x \leq 0.29$), and krupkaite $CuPbBi_{3-x}S_{6-1.5x}$ ($0 \leq x \leq 0.4$) (Harris & Chen 1976). Even though Harris & Chen (1976) found streaking in some of their X-ray-diffraction patterns, they do not appear to have considered that compositional ranges could be due to the disordered intergrowth of various types of ribbons. They attributed the streaks to 'stacking' disorder of aikinite units. The streaking can equally well be interpreted as due to the disordered intergrowth of a number of krupkaite ribbons within an aikinite matrix. Such an inter-

growth would also result in a significant variation from the ideal composition, which indeed they reported.

Springer (1971) reported complete solid-solution between bismuthinite and aikinite above 300°C in synthetic studies. He was unable to prepare the ordered intermediate phases, even after annealing for up to 3 months, and concluded that the process of chemical segregation leading to formation of super-structures can only occur below 300°C. Clearly in nature both mechanisms, solid solution and the dis-ordered intergrowth of ordered structure units, may operate.

But the nature of compositional variation in the bismuthinite–aikinite series clearly warrants further work. With the new generation of high-resolution analytical electron-microscopes, and better image simulation, it should be possible to determine the mechanism of compositional variation in these minerals.
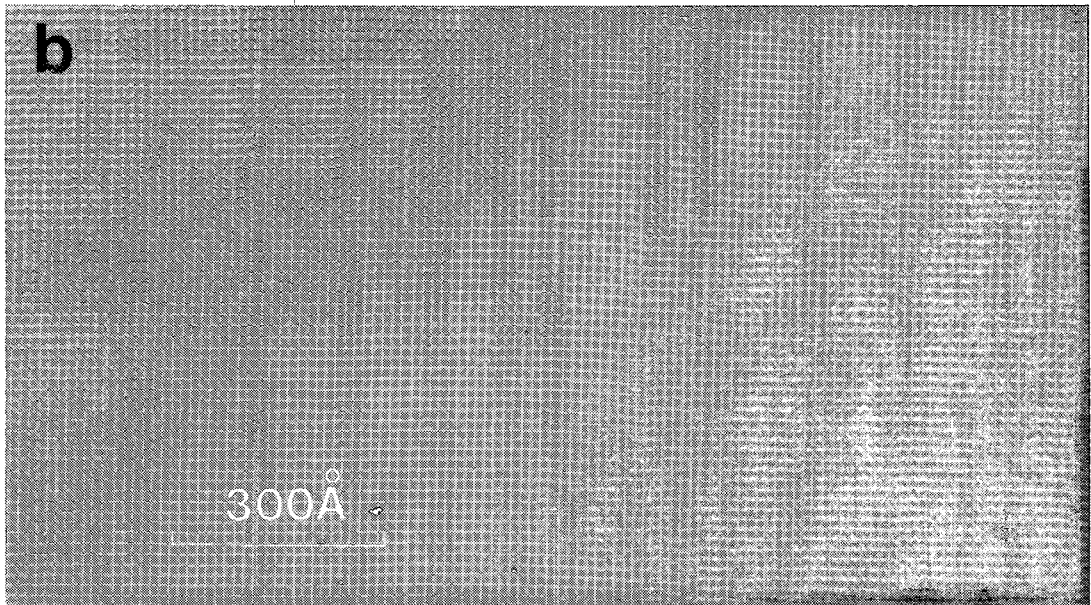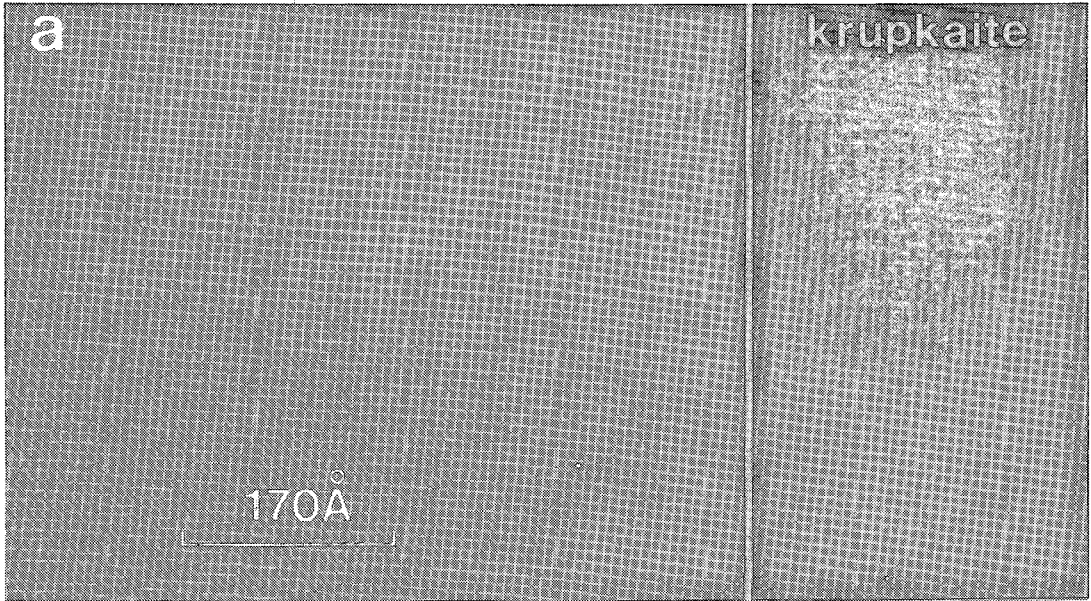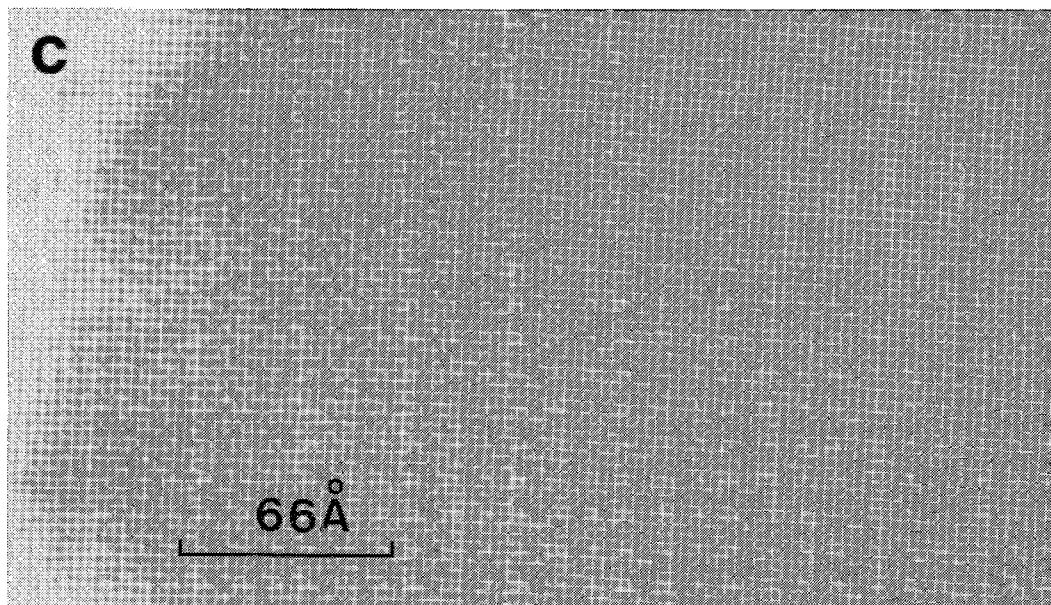
FIG. 4. High-resolution electron-microscope images of lindströmite (type material) down [001]. (a) Well-ordered region of lindströmite. Note the perfect ordering of the aikinite and krupkaite units to a 5a supercell. On the right of the image is a lamella of krupkaite 200 Å wide. (b) Disordered intergrowth of krupkaite and aikinite units. Note reversal of contrast from (a) due to thickness effects. (c) Well-ordered crystal of hammarite showing 3a repeat.
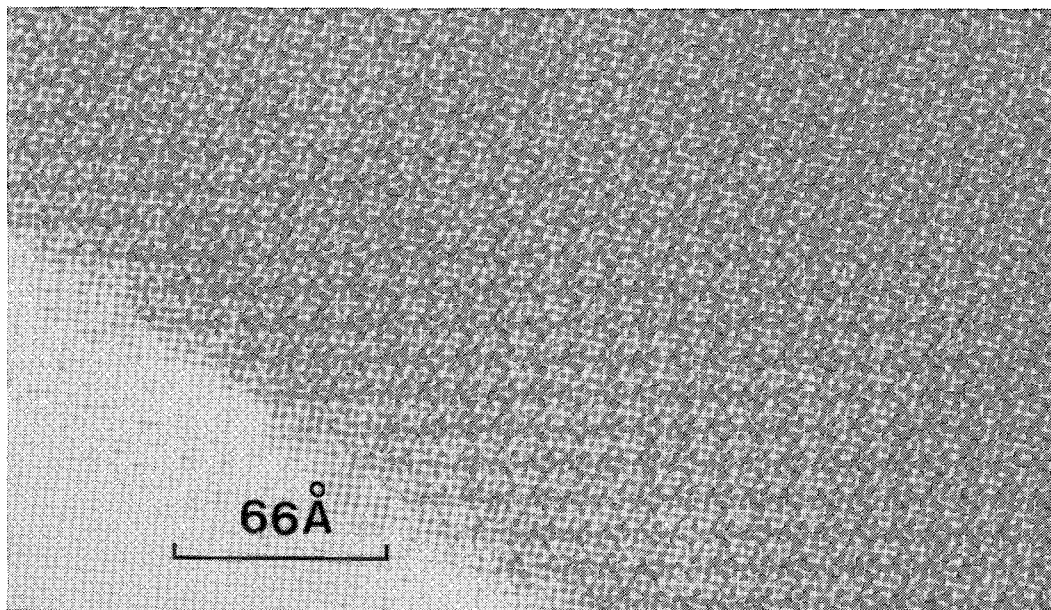

FIG. 5. Lattice image of krupkaite taken down the [001] zone.

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