Acta Cryst. (1991). A47, 405-413

Modulation Mechanism and Disorder Structure in Hollandite-Type Crystals

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(*Received* 24 *August* 1990; *accepted* 28 *January* 1991)

Abstract

The structural modulation in some hollandite-type crystals is explained by a vacancy-displacive modulation model. In this model the large cations located in the tetragonal channels along the *c* axis deviate from the average position to form a modulation wave. Three types of disorder in the initial phase of the modulation wave have been introduced to interpret apparently different diffraction patterns in hollandite-type crystals. A mathematical analysis as well as optical diffraction give results similar to those experimentally observed. High-resolution transmission electron microscope images have been observed to confirm the discussion further.

1. Introduction

Since the first paper on the crystal structure of hollandite $A_{2-y}B_{8-z}X_{16}$ (A: large cations such as Ba^{2+} and K^+; B: small and medium-sized cations such as Mn^{4+} and Fe^{3+}; X: O^{2-} and OH^-) (Bystrom & Bystrom, 1950), many related works have been reported (Sinclair, McLaughlin & Ringwood, 1980; Bursill, 1979; Mukherjee, 1960). The crystal has tetragonal or monoclinic symmetry and its structure consists of BO_6 octahedra sharing an edge and a corner to form a tetragonal channel along the *c* axis. The large cations, such as Ba and K, occupy the tetragonal channels. Satellite spots caused by a modulation wave and diffuse diffraction lines caused by a disordered structure have frequently been observed from hollandite crystals. It has been assumed that both the modulation and the disorder structure are produced depending on the arrangement of the cations in the tetragonal channels and that the origins of the modulation structure and the disorder structure were independent of each other.

Bursill & Grzinic (1980) studied the modulation structure in hollandites by high-resolution electron microscopy and proposed a short-range-ordered intergrowth model to explain the modulation phenomenon. Zandbergen, Everstijn, Mijlhoff, Renes & Ijdo (1977) studied a series of hollandites $A_xM_{4-y}N_yO_8$ with different x and found that the modulation wavelength was correlated with x. Based on this result they proposed an occupation wave model. Wu, Li, Ma & Shi (1990) and Wu, Li & Hashimoto (1990) have studied ankangite, $Ba_{0.827}(Ti_{5.827}V_{2.294}Cr_{0.053})O_{16}$, which has a structure essentially of hollandite type by electron diffraction analysis and proposed a vacancy-displacive modulation model, in which the modulation structure is produced through the arrangement of the channel cations.

Diffuse scattering lines normal to $\mathbf{c}^*$ have been observed in X-ray and electron diffraction patterns (EDPs) from many hollandite-type crystals (Dryden & Wadsley, 1958; Mukherjee, 1964; Beyeler, 1976; Sinclair *et al.*, 1980; Post, Von Dreele & Buseck, 1982; Terauchi, Futamura, Ishii & Fujiki, 1984; Suzuki, Tanaka, Ishigame, Suemoto, Shibata, Onoda & Fujiki, 1986; Zandbergen, Everstijn, Mijlhoff, Renes & Ijdo, 1987; Watanabe, Fujiki, Yoshikado & Ohachi, 1988, 1989; Wu, Li & Hashimoto, 1990). Undoubtedly, these lines indicate the presence of structural disorder. Beyeler (1976) pointed out that the diffraction streaks were caused by the arrangement of large cations, which lost the correlations between the different tetragonal channels. Grzinic (1985) calculated the diffraction intensities of K-hollandite from a model with a random mixture of cells. Post & Burnham (1986) studied hollandite by structure-energy calculations and suggested that the octahedral cations were probably disordered.

Different types of X-ray and electron diffraction patterns have been observed in different hollandites. Zandbergen *et al.* (1987) and Bursill & Grzinic (1980) showed diffraction patterns with sharp satellite spots. In many cases, however, only the streaks were observed in diffraction patterns (Dryden & Wadsley, 1958; Mukherjee, 1964; Beyeler, 1976; Sinclair *et al.*, 1980; Post *et al.*, 1982; Terauchi *et al.*, 1984; Zandbergen *et al.*, 1987; Watanabe *et al.*, 1988, 1989).

0108-7673/91/040405-09$03.00

Table 1. *Chemical compositions and lattice parameters of five synthetic specimens and the values of modulation wavelength q in the c* direction*

Composition	Symbol	a (nm)	c (nm)	x	q
$Cs_{1\cdot18}Mg_{0\cdot59}Ti_{7\cdot41}O_{16\cdot00}$	CMTO	1·01	0·289	1·18	0·32
$Rb_{1\cdot46}(Mg_{0\cdot73}Ti_{7\cdot27})O_{16\cdot00}$	RMTO	1·02	0·297	1·46	0·22
$Rb_{1\cdot49}(Al_{1\cdot69}Ti_{6\cdot35})O_{15\cdot92}$	RATO	1·01	0·293	1·49	0·26
$K_{0\cdot74}Ba_{0\cdot69}Al_{2\cdot12}Ti_{5\cdot88}O_{16\cdot00}$	KBATO	1·00	9·297	1·43	0·35
$K_{0\cdot84}Ba_{0\cdot50}Mg_{1\cdot00}Ti_{7\cdot00}O_{15\cdot92}$	KBMTO	1·01	0·297	1·34	0·33

However, Cadee & Prodan (1979), Suzuki *et al.* (1986), Zandbergen *et al.* (1987) and Wu, Li & Hashimoto (1990) reported that in some hollandites the sharp satellite spots and the diffuse scattering lines occurred in an EDP simultaneously. An important fact is that all satellite spots locate at the streaks. This implies that the disordered structure is related to the modulation structure. Wu, Li & Hashimoto (1990) proposed a model of vacancy-displacive modulation with an initial phase disorder (IPD) in order to explain the diffraction patterns of ankangite. Recently, Wu & Horiuchi (1991) have proved not only mathematically but also with the aid of optical diffraction that the IPD model can explain the diffraction streaks.

In this work we studied five synthetic priderite crystals with hollandite-type structure (Table 1) by transmission electron microscopy (TEM). The modulation mechanism for the hollandites is discussed with a vacancy-displacive model. It will be shown that the three types of diffraction patterns mentioned above are excited and explained based on the different conditions of IPD. The high-resolution TEM images are also shown to confirm the discussion.

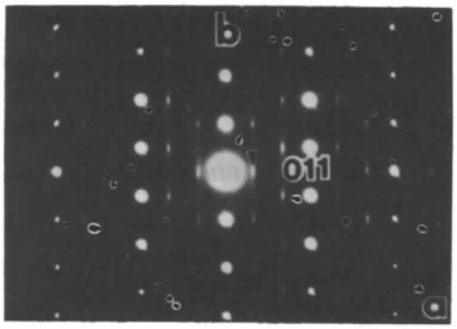
2. Experimental

A variety of single crystals of priderite with hollandite-type structure were grown from a flux melt as superionic conductors (Fujiki, Takenouchi, Onoda, Watanabe, Yoshikado, Ohachi & Taniguchi, 1987). Five bar-like crystals, CMTO, RMTO, RATO, KBATO and KBMTO, were selected from them as specimens in the present study. The lattice parameters are listed in Table 1.

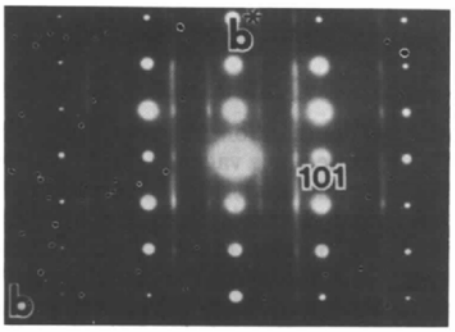
Conventionally fractured specimens were observed by the TEM, JEM-2000EX, operated at the accelerating voltage of 200 kV.

3. Electron diffraction patterns

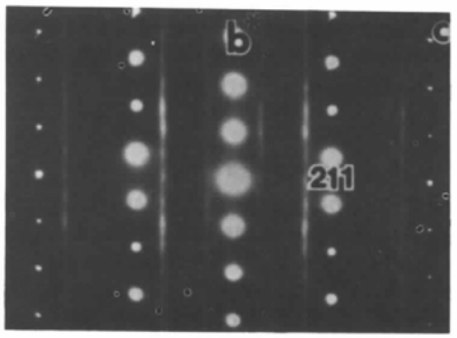
Figs. 1(*a*), (*b*), (*c*) and (*d*) show the EDPs taken from CMTO with the incident beam along [100], [1$\bar{1}$0], [1$\bar{2}$0] and [1$\bar{3}$0], respectively. The satellite spots produced by the modulation wave can be seen in Figs. 1(*a*) and (*c*). The modulation wave vector is $\mathbf{q} = \mathbf{c}^*/3{\cdot}12$. All the satellite spots locate on the streaks parallel to $\mathbf{b}^*$. The streaks can be seen in every EDP,



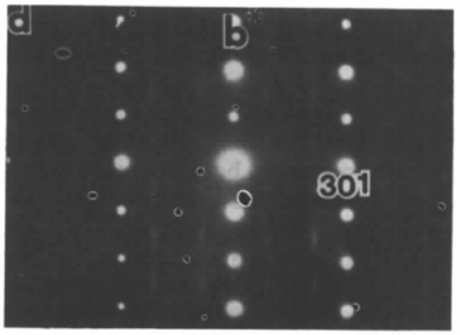
(*a*)



(*b*)



(*c*)



(*d*)

Fig. 1. The EDPs taken from a CMTO crystal along (*a*) [100], (*b*) [1$\bar{1}$0], (*c*) [1$\bar{2}$0] and (*d*) [1$\bar{3}$0]. All the satellite spots locate on the diffraction streaks. The satellite spots marked by an arrow can be expressed as 0001 with a four-dimensional index.

indicating that there are some reflection planes parallel to ($\mathbf{a}^*$, $\mathbf{b}^*$) in the reciprocal space.

Figs. 2(*a*), (*b*), (*c*) and (*d*) show a set of EDPs taken from RMTO along [100], [1$\bar{1}$0], [1$\bar{2}$0] and [1$\bar{3}$0], respectively. There are only diffraction streaks parallel to the ($\mathbf{a}^*$, $\mathbf{b}^*$) plane in every EDP with no clear satellite spots.

4. Vacancy-displacive modulation model

Wu, Li & Hashimoto (1990) have analyzed the EDPs taken from ankangite in detail and concluded that vacancy-displacive modulation occurs in the crystal. Recently, this model has been confirmed quantitatively by means of direct-methods analysis of electron diffraction (Xiang, Fan, Wu, Li & Pan, 1990). Now we believe that this model holds not only for ankangite but also for other crystals with hollandite-type structure because of the following reason as well as others pointed out previously.

Both from the local intergrowth model proposed by Bursill & Grzinic (1980) and from the occupation wave model proposed by Zandbergen *et al.* (1987), we infer that the modulation wavelength in holandites $A_xB_8O_{16}$ should depend only on the value of x. In other words, for any two hollandite crystals consisting of different species of cation but with the same value of x the modulation wavelengths should be equal or very close. However, this inference cannot be supported by the present experimental results. Table 1 shows that there is no definite correlation between q and x in five hollandite-type crystals. In this table, the values of q for the first four crystals are determined from the diffraction streaks. The correlation between the modulation wave vector and the streaks will be shown in the next section.

On the other hand, the vacancy-displacive model gives a different prospect. In this model there are some vacancies in the tetragonal channels. The interaction between adjacent cations in a channel is sometimes so strong that the channel cations can deviate from their average position along the c axis by as far as the sum of the radius of the large cations and an oxygen atom, which is part of the framework, is smaller than the radius of the tetragonal channels. The amount of deviation is denoted by a periodic function, which defines a displacive modulation structure. Firstly, the interaction should be related to the distance between the cations as well as to their valence. Secondly, the cations in the channel are not completely free from their surroundings, *i.e.* there must be interaction between framework and cations. This interaction will change according to the width of the channels as well as the size of the cations. Therefore, the modulation function depends on at least three factors: (1) the distance ($\sim 2c/x$) between the large cations in the same channel; (2) the cation

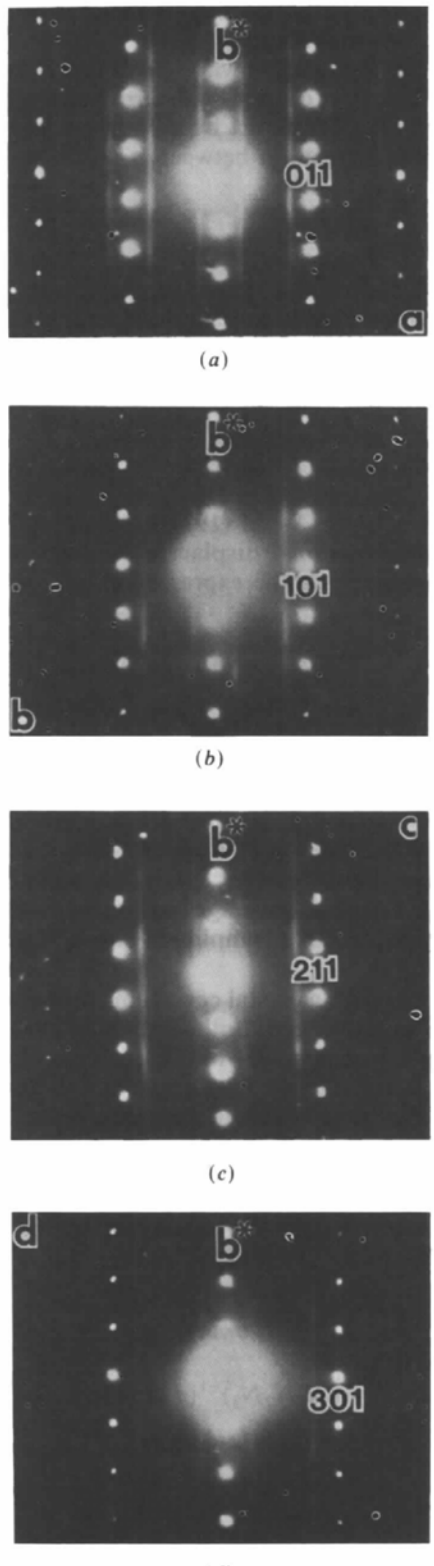


Fig. 2. The EDPs taken from RMTO along (*a*) [100], (*b*) [1$\bar{1}$0], (*c*) [1$\bar{2}$0] and (*d*) [1$\bar{3}$0]. Only the diffraction streaks appear in every EDP.

species (size, charge) occupying the channel; and (3) the framework structure.

Since the modulation wavelength is thus related to several factors, it cannot be determined simply from the value of x. This must be the reason why there is no definite correlation between q and x in Table 1.

5. IPD model

Wu, Li & Hashimoto (1990) suggested that the IPD model may be used to explain the streaks in the EDPs. In IPD the initial phase of the modulation wave is disordered for each channel. In other words, the positions of large cations along the c axis are different from channel to channel.

The effect of the IPD on the reciprocal space can be discussed mathematically. According to the formula given by de Wolff (1974), the structure factor of a one-dimensional displacive modulation with a sinusoidal wave can be expressed as

$$F(hklm)=\sum_j f_j \exp 2\pi i[hx_{j0}+ky_{j0}+lz_{j0} + m(\alpha_j+\tfrac{1}{2})]J_m(2\pi \mathbf{g}\cdot\mathbf{u}_{j0}), \quad (1)$$

where f_j is the atomic scattering factor of the jth atom, J_m is the mth-order Bessel function, $\mathbf{g}=\mathbf{H}+m\mathbf{q}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{q}$ is the diffraction vector in reciprocal space, $\mathbf{q}=q_1\mathbf{a}^*+q_2\mathbf{b}^*+q_3\mathbf{c}^*$ is the modulation wave basic vector, m is an integer, $\mathbf{r}_{j0}=x_{j0}\mathbf{a}+y_{j0}\mathbf{b}+z_{j0}\mathbf{c}$ is the average position of the jth atom, $\mathbf{u}_{j0}$ is the displacement amplitude and α_j is the initial phase.

Let us consider a crystal containing only two atoms A and B in a unit cell. Both of them are modulated by a displacement wave with the same wave vector $\mathbf{q}$ which is parallel to $\mathbf{c}^*$. If atoms A and B are modulated by the wave with initial phases

$$\alpha(n_1, n_2) \quad \text{and} \quad \beta(n_1, n_2), \quad (2)$$

respectively, the intensity of the diffraction pattern (Wu & Horiuchi, 1991) is

$$\begin{aligned} I(uvwm) &\propto \left|\sum_n^N F(uvwm)\right|^2 \\ &= (N_1N_2N_3)^{-1}\{f_A^2J_m^2(2\pi\mathbf{g}\cdot\mathbf{u}_{A0})T_1 \\ &\quad +2f_Af_BJ_m(2\pi\mathbf{g}\cdot\mathbf{u}_{A0}) \\ &\quad \times J_m(2\pi\mathbf{g}\cdot\mathbf{u}_{B0})\,\mathrm{Re}\,[T_2C] \\ &\quad +f_B^2J_m^2(2\pi\mathbf{g}\cdot\mathbf{u}_{B0})T_3\}, \end{aligned} \quad (3)$$

where $C=\exp 2\pi i[\mathbf{H}\cdot(\mathbf{r}_{A0}-\mathbf{r}_{B0})]$ means a constant phase factor, N_1, N_2 and N_3 are the numbers of unit cells along the three principal axes, Re is the real part of the contents of the brackets, $\mathbf{H}=u\mathbf{a}^*+v\mathbf{b}^*+w\mathbf{c}^*$, the vector in reciprocal space, and

$$\begin{aligned} T_1 &= \sum_{n,n'}^N \exp 2\pi i\{\mathbf{H}\cdot(\mathbf{R}-\mathbf{R}') \\ &\quad +m[\alpha(n_1, n_2)-\alpha(n_1', n_2')]\} \\ &= N_3^2\delta_{wl}\sum \exp 2\pi i\{u(n_1-n_1')+v(n_2-n_2') \\ &\quad +m[\alpha(n_1, n_2)-\alpha(n_1', n_2')]\} \end{aligned} \quad (4)$$

$$\begin{aligned} T_2 &= \sum \exp 2\pi iw(n_3-n_3') \\ &\quad \times\sum \exp 2\pi i[u(n_1-n_2')+v(n_2-n_2') \\ &\quad +m\alpha(n_1, n_2)-m\beta(n_1', n_2')] \\ &= N_3^2\delta_{wl}\sum \exp 2\pi i[u(n_1-n_1')+v(n_2-n_2') \\ &\quad +m\alpha(n_1, n_2)-m\beta(n_1', n_2')] \end{aligned} \quad (5)$$

$$\begin{aligned} T_3 &= N_3^2\delta_{wl}\sum \exp 2\pi i\{u(n_1-n_1')+v(n_2-n_2') \\ &\quad +m[\beta(n_1, n_2)-\beta(n_1', n_2')]\} \end{aligned} \quad (6)$$

where $\mathbf{R}=n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c}$ (n_1, n_2, n_3: integer), $N=(N_1, N_2, N_3)$, $\mathbf{n}=(n_1, n_2, n_3)$ and δ is the delta function.

It is clear that the structure of reciprocal space will be determined by T_1, T_2 and T_3. The results obtained from (4), (5) and (6) will be different depending on $\alpha(n_1, n_2)$ and $\beta(n_1, n_2)$ as follows.

(a) Both $\alpha(n_1, n_2)$ and $\beta(n_1, n_2)$ are constant

In this case all atoms are modulated by the plane wave. From (4), (5) and (6) we can obtain

$$\begin{aligned} T_1 &= T_2 = T_3 \\ &= (N_1N_2N_3)^2\delta_{uh}\delta_{vk}\delta_{wl} \quad (h, k, l: \text{integer}). \end{aligned}$$

This means that there are only sharp satellite spots in the reciprocal space.

(b) $\alpha(n_1, n_2)$ is constant and $\beta(n_1, n_2)$ is random

In this case we obtain from (4)

$$T_1=(N_1N_2N_3)^2\delta_{uh}\delta_{vk}\delta_{wl} \quad (h, k, l: \text{integer}).$$

This means that the first term of (3) gives sharp diffraction spots. However, T_2 and T_3 are complicated. It can be found from (5) and (6) that T_2 and T_3 are nonzero only on the planes whose index w is integer. On the other hand, there is no limitation on the other two indexes. It means that some continuous reflection planes parallel to $(\mathbf{a}^*, \mathbf{b}^*)$ occur in the reciprocal space, which are a distance mq from every diffraction plane $l=$ integer.

According to the results, we know that the atoms in the different channels modulated by the wave with the same initial phase contribute to sharp satellite diffraction spots, while the atoms modulated by the wave with a random initial phase contribute to diffuse reflections. The satellite spots always locate on the diffuse reflection.

(*c*) *Both* $\alpha(n_1, n_2)$ *and* $\beta(n_1, n_2)$ *are random*

In this case, all of (4), (5) and (6) excite the reflection planes which are parallel to $(\mathbf{a}^*, \mathbf{b}^*)$ and a distance mq from diffraction planes with l = integer.

However, when $m = 0$, it is found from (4) to (6) that for any values of $\alpha(n_1, n_2)$ and $\beta(n_1, n_2)$ we have

$$T_1 = T_2 = T_3 = (N_1 N_2 N_3)^2 \delta_{uh} \delta_{vk} \delta_{wl}.$$

This means that no streaks occur in the planes passing through the fundamental diffraction spots. The fundamental spots are always sharp, no matter how the initial phase is.

As a result, there are three possible types of reciprocal space for displacive modulation structures. (1) There are only sharp satellite spots in reciprocal space. This corresponds to the initial phase being completely ordered. (2) There are some sharp satellite spots as well as some streaks. The satellite spots always locate on the streaks. This corresponds to the initial phase being partially disordered. (3) Streaks arise only besides fundamental diffraction spots. The streaks locate at a distance mq from the plane $(00l)$. This corresponds to complete initial phase disorder. All these three types have been observed in the hollandite-type crystals mentioned above.

Optical diffraction is a convenient method to confirm the validity of the IPD model. The simple two-dimensional displacive modulation models shown in Figs. 3(*a*) and (*c*) satisfy the following conditions: (1) the unit cell is a simple square, $a = b$; (2) it is composed of only two atoms, *A* and *B*, indicated by dots and open circles, in a unit cell and their average positions are (0, 0) and $(\frac{1}{2}, \frac{1}{2})$, respectively; (3) both of them are modulated by the waves with the same wave vector $\mathbf{q} = \mathbf{a}^*/2{\cdot}3$ and amplitude; (4) in Fig. 3(*a*) the initial phase is constant for all atoms, while in Fig. 3(c) it is constant for *A* atoms but changes randomly between 0 and 20° for *B* atoms.

The optical diffraction patterns (ODPs) corresponding to Figs. 3(*a*) and (*c*) are shown in (*b*) and (*d*), respectively. In Fig. 3(*b*) only the sharp satellite spots can be seen, while in (*d*) the streaks passing through the satellite spots are added. These two patterns are what was expected in advance.

It should be noticed, however, that the model we used here is a little different from the real structure of hollandite. In the model we proposed two kinds of atoms, *A* and *B*, to be modulated. Under the conditions of *A* atoms orderly modulated and *B* atoms disorderly modulated, we get diffraction patterns like Fig. 3(*d*), in which the sharp spots like (001) come from *A* and the streaks come from *B*. On the other hand, in hollandite-type crystals only the large cations in the channels are modulated. We then consider that the cations play the roles not only of *A* but also of *B* at the same time. Both satellite spots and diffuse streaks in Fig. 1 are from the same species of cations in the different channels. In other words, the appearance of sharp spots and streaks means that the cations are only ordered locally.

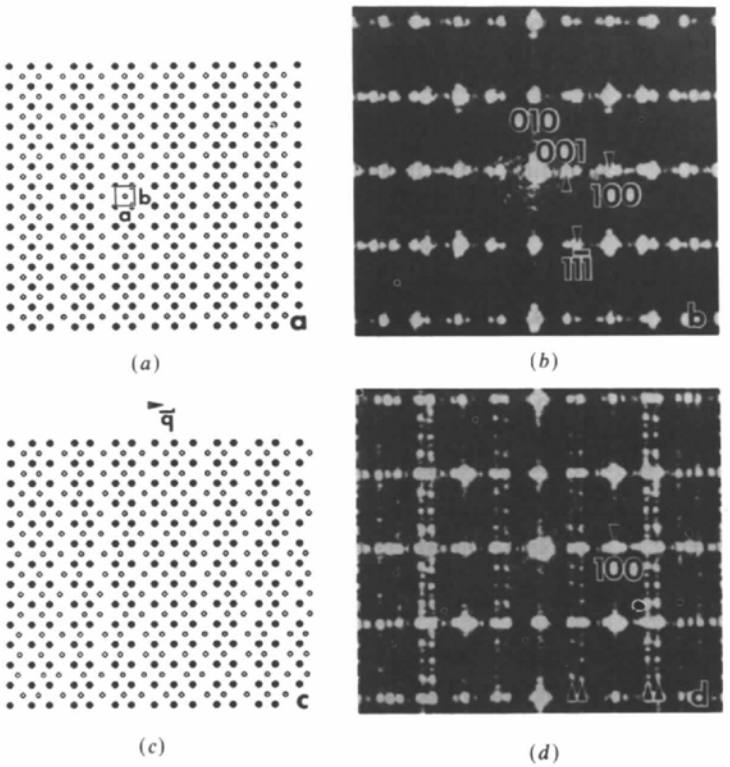


Fig. 3. Two-dimensional crystal models constructed from two atoms *A* and *B*, whose positions are indicated by dots and open circles, respectively. (*a*) The positions of both atoms are modulated by the plane wave propagating along the *q* direction with $\mathbf{q} = \mathbf{a}^*/2{\cdot}3$. The wavefront is perpendicular to $\mathbf{q}$. (*b*) The ODP corresponding to (*a*). Indexes *hkm* are indicated. (*c*) The positions of the *B* atoms are modulated by the wave with random initial phase between 0 and 20°, while those of the *A* atoms are modulated by a plane wave. (*d*) The ODP corresponding to (*c*). Diffraction streaks arise passing through satellite spots.

When the interaction between the cations in adjacent channels is strong enough, the initial phase of the modulation wave will be ordered, namely, $\alpha(n_1, n_2) = \text{constant}$ (Fig. 4*a*). We find only sharp satellite spots under this condition (Bursill & Grzinic, 1980). When the interaction is weak, on the other hand, the initial phase will be partially disordered, *i.e.* in some local areas the initial phase is ordered, while in some channels the initial phase is random (Fig. 4*b*). We then see the satellite spots as well as the streaks in the diffraction patterns as in Fig. 1(*a*). When the interaction is greatly shielded by the framework structure, the initial phase will be completely disordered (Fig. 4*c*) and only the streaks can be found, as we have observed in RMTO (Fig. 2).

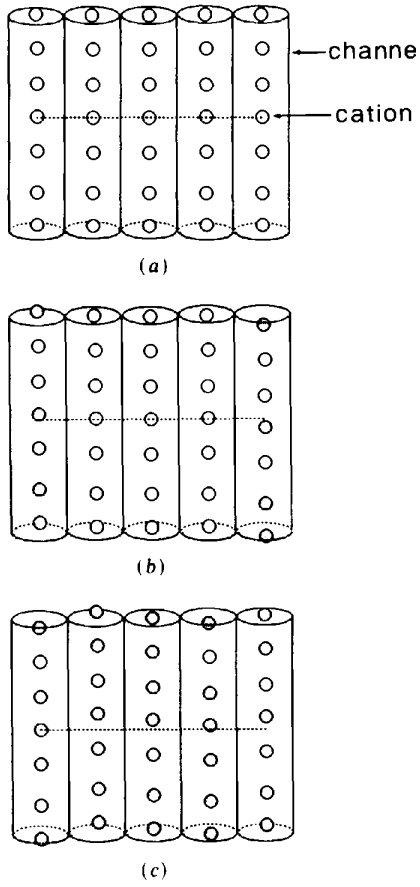


Fig. 4. A scheme to show three possible conditions for the initial phase due to the cation arrangement in the channels of hollandite-type crystals. (*a*) All cations in channels are modulated with the same initial phase and the modulation structure is perfectly ordered. (*b*) The open circles indicate the cations modulated with a constant initial phase, while the shadowed circles indicate the cations modulated with IPD. The former circles can be considered to act as *A* atoms and the latter as *B* atoms in Fig. 3(*c*). The initial phase is thus partially ordered. (*c*) The cations start with random initial phase in all channels, *i.e.* the initial phase is completely disordered.

6. High-resolution images

Fig. 5(*a*) is a high-resolution image taken from CMTO along $[\bar{1}11]$. The EDP and ODP corresponding to the image are shown in (*c*) and (*d*), respectively. White dots in Fig. 5(*a*) are seen periodically only in some local areas. In other large areas, the intensities as well as the spacings of the dots are different from region to region. For example, in the regions marked by small arrows the translational period is different from that in the surrounding area. The ODP (*d*) shows that there are some streaks in agreement with what we have observed in EDP (*c*). This means that the image carries information about the modulation structure. Indeed, the average distance between two strong white dots is almost three times that between two closed white dots along $[1\bar{1}2]$, while from (*c*) it is found that the line *S* locates at about one third of the distance between the main diffraction layers $l = 0$ and $l = 1$. However, except in some local areas, the strong white dots are not arranged in a line along [110]. This can be seen much more clearly in Fig. 5(*b*), which is taken with a small objective aperture and in which the main diffraction beams with $l \neq 0$ never contribute to imaging. It implies that the dots in this image are related only to the periodicity in the modulation. Evidently, except in some small areas indicated by the arrows, most of the dots are not in a line along [110]. Equivalently, the ODP (*e*) taken from (*b*) shows that streaks parallel to [110] occur. The streak *S* has its intensity maximum near to that of the main spots $l = 0$, while *R* its intensity maximum near to that of the main spots $l = 1$.

Fig. 6(*a*) is an image taken from CMTO. The specimen was tilted around the *b* axis so that only one streak was included in the objective aperture. Figs. 6(*b*) and (*c*) are an EDP and an ODP corresponding to the image. Undoubtedly, the dots in the image relate only to the modulation structure. In the regions indicated by the arrows, the dots are in a line along the *b* direction. This means that in some channels the modulation waves start with same initial phases. These modulation waves produce the contribution to form the sharp satellite spots. On the other hand, the dots are not always in a line. This means that in some channels the initial phases are different from each other, which contributes to the streaks in the diffraction patterns, as we predicted in the last section.

Fig. 7 is an image taken from RMTO along the *a* axis. Some imperfect fringes indicated by the arrows can be seen clearly. These fringes are roughly parallel to the *b* axis, but slightly curved. This means that the modulation wave propagating along the *c* axis is not a plane wave. The spacing between the fringes is approximately equal to the modulation wavelength.

Fig. 8 is taken with a smaller objective aperture along $[\bar{1}11]$. The corresponding ODP inserted in the

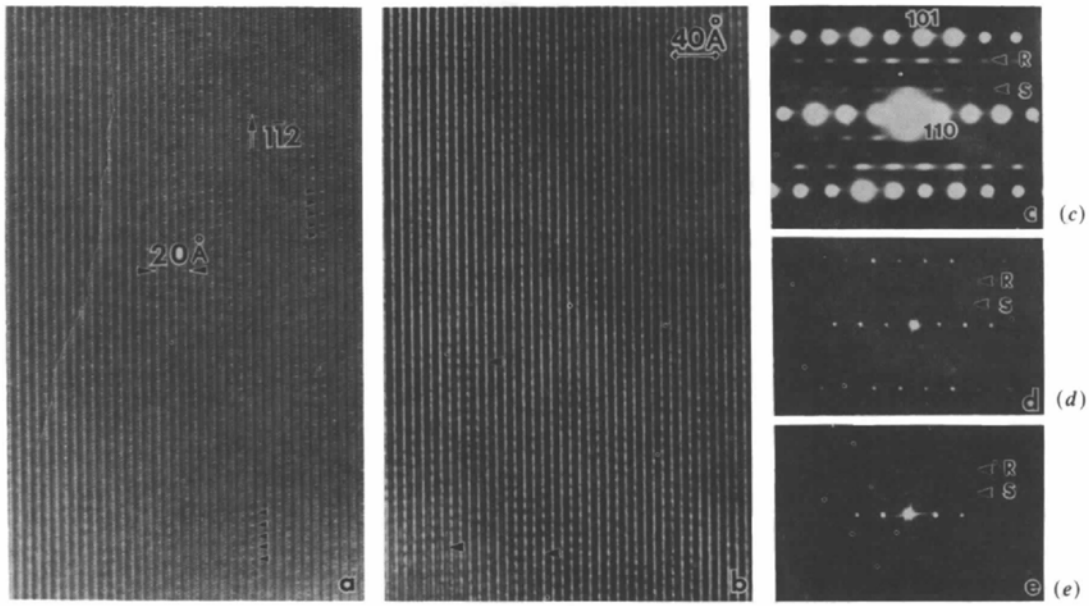


Fig. 5. (*a*) High-resolution TEM image taken from CMTO along [$\bar{1}11$]; (*b*) the image taken with a smaller objective aperture; (*c*) the corresponding EDP; (*d*) and (*e*) are ODPs corresponding to (*a*) and (*b*), respectively. The intensities and the spacings of the dots indicated by the small arrows are different from those of their neighbors. It can be understood from (*d*) that this change is related to the modulation structure. Owing to the initial phase disorder the modulation wave is not a perfect plane wave; this is more easily seen from (*b*). Subsequently, the streaks are observed in ODP (*e*).

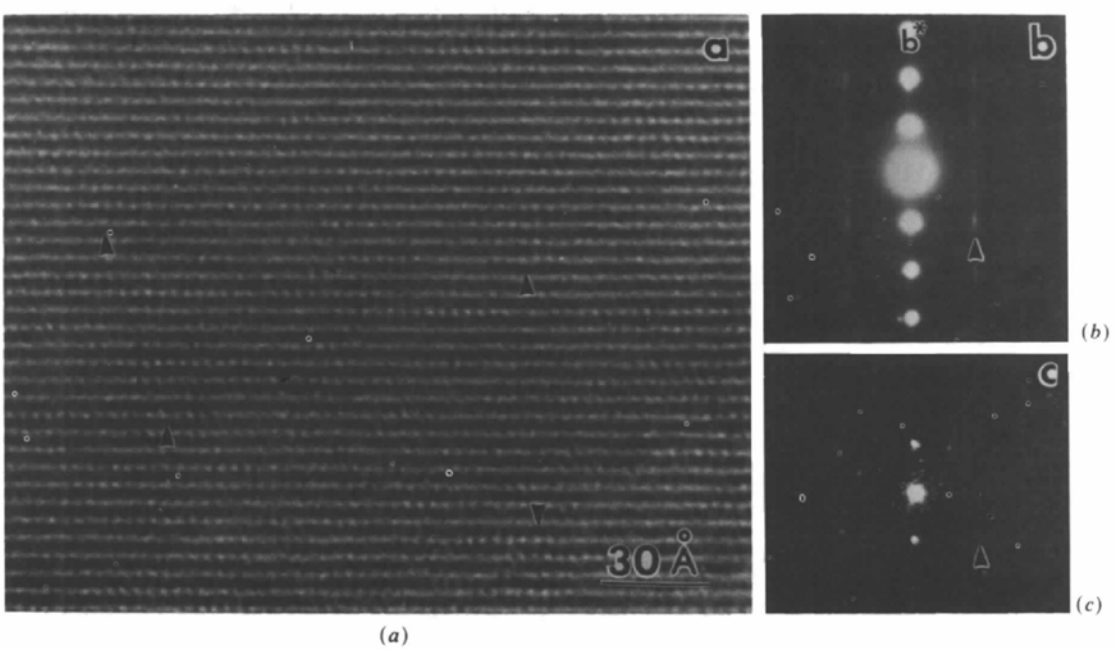


Fig. 6. (*a*) A high-resolution image taken from CMTO with a smaller objective aperture. (*b*) and (*c*) are the EDP and ODP corresponding to the image. In some regions, indicated by arrows, the dots are in a line along the *b* direction. These regions contribute to the satellite spots in the ODP. It is easy to recognize that the modulation wave is not always in the same phase, so it forms the streaks in the ODP.

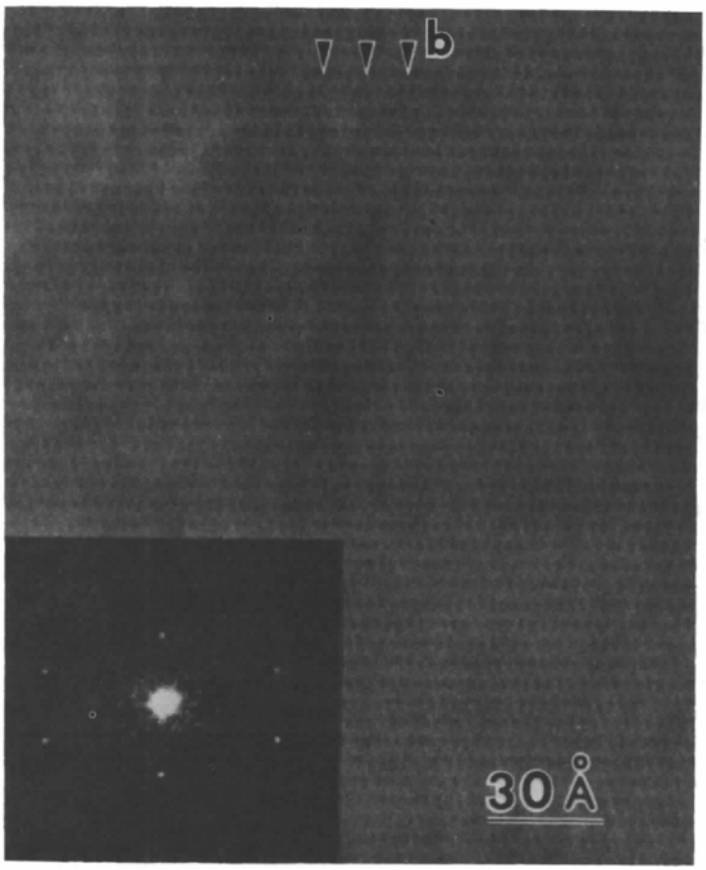


Fig. 7. A high-resolution image taken from RMTO along [100]. The fringes corresponding to the modulation structure are indicated by the arrows. The fringes are always zigzag, showing that the modulation wave is not in the same phase.

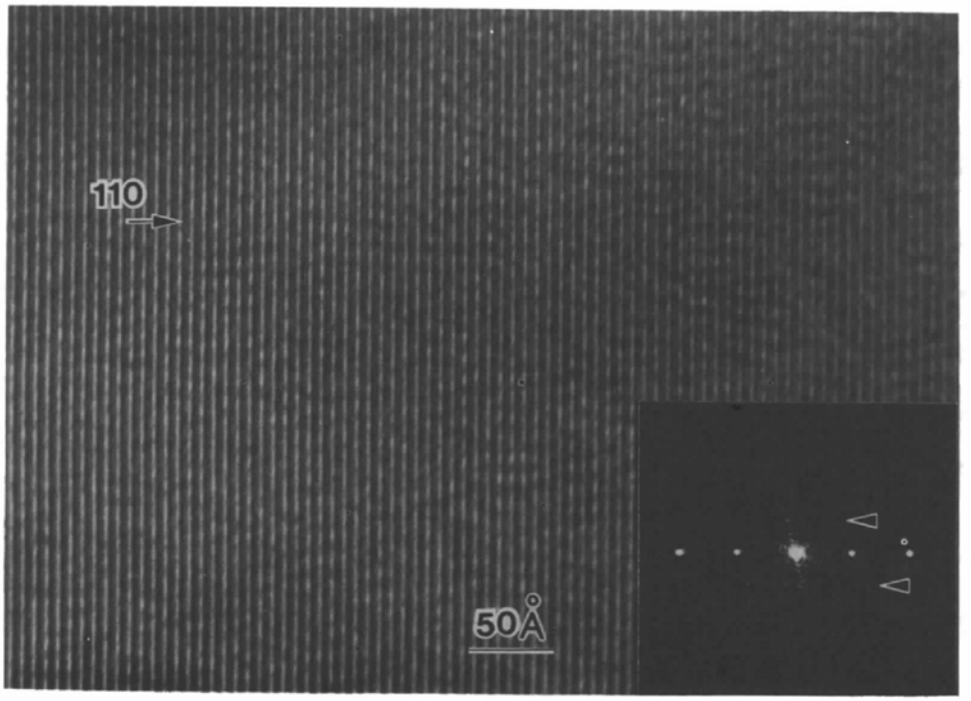


Fig. 8. An image taken from RMTO along [111] with a smaller objective aperture. The fringes are always curved. It is difficult to see the dots in the image. From the inserted ODP it is known that the fringes are related to the modulation structure. It is evident that the modulation wave is not a plane wave.

image shows that along the direction normal to (110)* only streaks contribute to the image. This image is very different from Fig. 6(*a*). In local regions of Fig. 6(*a*), dots arranged in a line can be seen. This means that in some of the channels the modulation wave is plane, which contributes to the satellite spots in the ODP. But in this image the fringes with a distance from each other of about 1·3 nm, which can be seen in the [110] direction, are always curved. This means that there is no plane modulation wave in the crystal. Therefore, there are only streaks in the ODP. On the other hand, almost no sharp dots can be seen in this image. This is also different from the case of CMTO. The reason must be as follows: in CMTO the modulation wave is in the same phase for some channels so that the projections of the modulation wave sometimes coincide with each other, which corresponds to the dots observed in Fig. 6. However, in RMTO the initial phase of the modulation wave is completely disordered, *i.e.* the projections of the modulation wave in different channels seldom coincide with each other. When the specimen is thinner, the projections of the disordered modulation wave give an image like this one which shows some fringes, but when the specimen is thick enough, only a line with almost uniform contrast can be observed in the image.

7. Summary

A vacancy-displacive modulation model is used to explain the modulation mechanism for hollandite-like crystals. It is proposed that the large cations located in the tetragonal channels deviate from the average position along the *c* axis to form a modulation wave. The modulation period will depend on the degree of occupation, the species of cations and the structure of the framework. The results obtained from the composition analysis as well as the electron diffraction analysis confirm the validity of this model.

Three types of diffraction patterns obtained from some hollandite-like crystals are explained by the different conditions in the initial phase of the modulation wave. When the initial phase is identical for each channel, the modulation wave gives the sharp satellite spots in the diffraction pattern. When the initial phase is partially disordered, the sharp satellite spots as well as the streaks are seen in the same diffraction pattern. When the initial phase is completely disordered, only the streaks are found in the diffraction pattern. ODPs obtained from the IPD model are in good agreement with this conclusion.

The IPD model is also supported by the high-resolution images taken from two typical hollandite-type crystals, CMTO and RMTO. The former corresponds to the initial partially disordered phase, the latter corresponds to the initial completely disordered phase. Owing to the partial disorder of the initial phase, perfect modulation fringes cannot be seen in the image of CMTO except in some local areas. Almost no dots can be seen in the image taken from RMTO with small aperture. This is because the initial phase of the modulation wave is variable from channel to channel.

The authors thank Dr M. Watanabe for valuable discussions. XJW expresses his sincere appreciation to the Science and Technology Agency, Japan, for offering the fellowship.

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