Diffuse Scattering from $YBa_2Cu_3O_{7-\delta}$ Oxide Caused by Magneli-Type Plane Defects

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It is shown that if a periodical faulting of the double-period orthorhombic $(\frac{1}{2}00)$ phase in $YBa_2Cu_3O_{7-\delta}$ produces a Magneli series, $YBa_2Cu_3O_{7-n/(2n+1)}$, with regular superlattice spots at $[\frac{1}{2} \pm 1/2(2n+1),0,0]$, the random faulting results in either broadening of the $(\frac{1}{2}00)$ diffraction maximum or its splitting into two maxima, $(\frac{1}{2} \pm \epsilon,0,0)$, depending on the stoichiometry. The observation of these effects is a strong argument in favor of an assumption that this compound is inherently inhomogeneous due to the accommodation of nonstoichiometry by means of the formation of interstitial plane defects.

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As it has been shown in our previous work,[1,2] at low temperature the nonstoichiometric high-temperature superconducting oxide, $YBa_2Cu_3O_{7-\delta}$, must either decompose into a mixture of completely ordered phases or congruently order forming a Magneli homologous series, $YBa_2Cu_3O_{7-n/(2n+1)}$ $(n=1,2,\ldots,\infty)$. The Magneli phases are long-period layer superstructures formed by alternation of oxygen-occupied and -vacant (100) planes separated by a crystal lattice parameter a. Their structure is specified by a stacking sequence of occupied (O) and vacant (□) layers. The period of the superstructure is $a_n = a(2n+1)$. It is determined by a nonstoichiometry parameter $\delta_n = n/(2n+1)$.[1] An example of an alternation of occupied and vacant planes for a Magneli phase with $n=3$ is given by the sequence

$$\ldots \square\underline{OO}\square O\square O\square\underline{OO}\square O\square O\square\underline{OO}\square \ldots . \quad (1)$$
$$\leftarrow 2n+1 \rightarrow$$

The series of homologous phases of the type (1) is, in fact, generated by a periodical distribution of interstitial plane defects, OO, underlined in (1). The defects are pairs of completely occupied nearest-neighbor plane layers separated by segments of the regular basic sequence

$$\ldots O\square O\square O\square O\square O\square O\square O\square O \ldots . \quad (2)$$

The structure described by the basic sequence (2) is a homologous double-period $(\frac{1}{2}00)$ phase $(n=\infty)$ with the composition $YBa_2Cu_3O_{6.5}$. The nth member of a homologous series with the stacking (1) produces the dominant diffraction spot at the $(n/(2n+1),0,0)$ generic points. The theory[1] is an extension of the theory[3] predicting the structure of the Ti_nO_{2n-1} and Mo_nO_{2n-1} Magneli series. Electron microscopic and diffraction data by Chen *et al.*,[4] Van Tandeloo, Zanderbergen, and Amelincky,[5,6] Werder *et al.*,[7] and Fleming *et al.*[8] confirm the existence of double-period $(n=\infty)$, triple-period $(n=1)$, and fivefold-period $(n=2)$ structural states in nonstoichiometric compounds $YBa_2Cu_3O_{7-\delta}$, where $0.5 < \delta < 0.7$.

If decomposition of the nonstoichiometric double-period $(\frac{1}{2}00)$ Magneli phase with $\delta > \frac{1}{2}$ is hindered at low temperature, the phase cannot reach the completely ordered state as is required by the third principle of thermodynamics. Then the excess oxygen atoms form interstitial plane defects, OO, pairs of nearest (100) planes fully occupied by oxygen atoms. The defects are separated by the segments of the double-period phase with the sequence (2). The defects may form both periodical (ordered) and random (disordered) distributions. A periodical repetition of the OO defects gives the Magneli-type series $YBa_2Cu_3O_{7-n/(2n+1)}$ discussed in Ref. 1. Random, disordered distributions of the defects may be expected when the diffusion rate is not sufficient to provide their ordering. An example of such a random distribution of the interstitial plane defects formed by faulting the regular double-period sequence of occupied and vacant layers, (2), is given by the following stacking sequence:

$$\ldots O\square\underline{OO}\square\underline{OO}\square O\square O\square O\square\underline{OO}\square O\square\underline{OO} \ldots .$$

The purpose of this paper is a theoretical investigation of the diffuse scattering generated by a random sequence of the interstitial OO defects in $YBa_2Cu_3O_{7-\delta}$. The comparison between the calculated and observed diffraction patterns may be an important source of information about the structure of the high-temperature superconducting $YBa_2Cu_3O_{7-\delta}$ oxides within the nonstoichiometric range and may help to interpret the available experimental data.

Intensity of diffuse scattering generated by the (100) interstitial plane defects.— Let us consider a stacking sequence of the (100) plane layers separated by the period a in the $YBa_2Cu_3O_7$ structure that are either completely occupied by oxygen atoms or completely vacant. The intensity profile along the [100] direction in reciprocal

space is described by the equation

$$I(h)=|f_{ox}|^2\sum_{pp'}\langle c(p)_{vac}c(p')_{vac}\rangle \times\exp[i2\pi h(p-p')], \quad (3)$$

where $c(p)_{vac}$ is a stochastic variable equal to 1 if a pth layer is vacant and equal to 0 if it is occupied by oxygen atoms, $q=2\pi h/a$ is the nonzero component of the diffraction vector $\mathbf{q}=(2\pi/a)(h,0,0)$, h is the coordinate in the reciprocal space along the [100] direction [$0<h<1$, the points $h=0$ and 1 are the fundamental reciprocal-lattice points (000) and (100) of the $YBa_2Cu_3O_7$ compound], and f_{ox} is the scattering factor of a completely occupied (100) layer; $\langle\cdots\rangle$ designates a spatial averaging along the sample, and summation is carried out over all planes of the crystal. It follows from Eq. (3) that the intensity distribution may be calculated if the correlator $\langle c(p)_{vac}c(p')_{vac}\rangle$ is known. If the interstitial defects do not form an ordered array, the correlator $\langle c(p)_{vac}c(p')_{vac}\rangle$ depends on the difference of coordinates of the layers, $m=p-p'$, and thus can be presented as $\bar{c}_{vac}P(m)^{vac}$, where $P(m)^{vac}$ is a conditional probability to have the mth layer vacant if the zeroth layer is certainly vacant, and $\bar{c}_{vac}$ is an absolute probability for a layer to be vacant which is equal to the fraction of the vacant layers. One may readily see that $\bar{c}_{vac}=\delta$, where δ is the nonstoichiometry parameter in the formula $YBa_2Cu_3O_{7-\delta}$. Using $\langle c(p)_{vac}c(p')_{vac}\rangle=\bar{c}_{vac}P(m)^{vac}$ and $\bar{c}_{vac}=\delta$ in (3) gives

$$I(h)=N|f_{ox}|^2\delta\sum_{m=-\infty}^{m=\infty}P(m)^{vac}\exp(i2\pi hm), \quad (4)$$

where N is a macroscopically large total number of layers. Equation (4) reduces the problem of determining the intensity distribution to the problem of determining the conditional probabilities, $P(m)^{vac}$.

Probabilities $P(m)^{vac}$.—Let us assume that plane defects, which are interstitial (100) layers, are randomly distributed along the direction of axis a. The only geometrical constraint which we impose on this distribution is the requirement that neither two vacant (100) layers nor two faults can be nearest neighbors. This means that a vacant layer is always followed by a completely occupied layer, and there are no groups with more than two completely occupied nearest-neighbor layers. The above constraint reflects the fact that the repulsive interaction makes the regular sequence (2) the most stable one. The faulting of this sequence caused by introducing extra oxygen planes is an inevitable effect which appears with deviation of stoichiometry from $\delta=0.5$. The formation of the OO faults separated by segments of the regular sequence (2) provides the least possible damage to this regular sequence.

To find the conditional probability $P(m)^{vac}$ we have to assume that the zeroth plane is vacant, i.e.,

$$P(0)^{vac}=1. \quad (5a)$$

Since two vacant layers cannot be nearest neighbors, the next layer ($m=1$) is certainly occupied, and thus

$$P(1)^{vac}=0. \quad (5b)$$

The relations (5) are the boundary conditions at $m=0$ and 1.

Let us also introduce the conditional probability $P(m)^{ox}$ to find the mth layer occupied if the zeroth layer is vacant. Since each layer is either occupied or vacant,

$$P(m)^{vac}+P(m)^{ox}=1. \quad (6)$$

We also introduce the constant probability α to have a OO fault in the regular sequence (2). Since the distribution of faults is assumed random, the probability α is a constant. The requirement that two vacant layers cannot be nearest neighbors imposes near-neighbor and next-near-neighbor correlation on the fault distribution. The probability $P(m)^{vac}$ can be derived by considering the balance between the $m-2$, $m-1$, and mth layers. The mth layer can be occupied by oxygen atoms only in two cases: if the $(m-1)$th layer is vacant, or if the $(m-2)$th layer is vacant but the $(m-1)$th layer is occupied.

These two possibilities are described by the following sequences:

(a) $\underset{m-2}{O}$ ——— $\underset{m-1}{\square}$ ——— $\underset{m}{O}$

(b) $\underset{m-2}{\square}$ ——— $\underset{m-1}{O}$ ——— $\underset{m}{O}$.

The probability that the mth layer is occupied in the sequence (a) is equal to the probability $P(m-1)^{vac}$ that the $(m-1)$th layer is vacant since the first event certainly produces the second one. The probability that the mth layer is occupied in the sequence (b) is equal to the probability that the $(m-1)$th layer is occupied [which is equal to the probability $P(m-2)^{vac}$ that the $(m-2)$th layer is vacant since a vacant layer is certainly followed by occupied layer] multiplied by the probability α that a fault appears at the mth layer. The resultant probability is $\alpha P(m-2)^{vac}$. It follows from the sequences (a) and (b) that the total probability $P(m)^{ox}$ that the mth layer is occupied is the sum

$$P(m)^{ox}=P(m-1)^{vac}+\alpha P(m-2)^{vac}.$$

This sum can be rewritten as

$$P(m)^{vac}+P(m-1)^{vac}+\alpha P(m-2)^{vac}=1 \quad (7)$$

if the condition (6) is used.

Equation (7) is a nonhomogeneous difference equation with the boundary conditions (5). It has the following two solutions:

$$P(m)^{vac}=\frac{1}{2+\alpha}+(b_1-b_2)[-\tfrac{1}{2}+(\tfrac{1}{4}-\alpha)^{1/2}]^m +(b_1+b_2)[-\tfrac{1}{2}-(\tfrac{1}{4}-\alpha)^{1/2}]^m, \quad (8a)$$

$$P(m)^{vac}=\frac{1}{2+\alpha}+b_1'(-\sqrt{\alpha})^m\cos(\phi m) +b_2'(-\sqrt{\alpha})^m\sin(\phi m), \quad (8b)$$

if $\alpha < \frac{1}{4}$ and $\alpha > \frac{1}{4}$, respectively, where $b_1 = (1+\alpha)/2(2+\alpha)$, $b_2 = (1-\alpha)/4(2+\alpha)(\frac{1}{4}-\alpha)^{1/2}$, $b_1' = (1+\alpha)/2(2+\alpha)$, $b_2' = (1-\alpha)/4(2+\alpha)(\alpha-\frac{1}{4})^{1/2}$, and $\phi = \arctan[(4\alpha-1)^{1/2}]$. It follows from (8) that as $m \to \infty$, $P(m)^{\text{vac}} \to 1/(2+\alpha)$. On the other hand, the conditional probability to find a vacant plane at $m=\infty$ should be equal to the absolute probability of this event, i.e., $P(\infty)^{\text{vac}} = 1/(2+\alpha) = \bar{c}_{\text{vac}} = \delta$. The relation $1/(2+\alpha) = \delta$ and its consequence

$$\alpha = (1-2\delta)/\delta \tag{9}$$

give a direct relation between the nonstoichiometry parameter δ and the probability of faulting, α, in this model. Using probabilities (8a) and (8b) in Eq. (5) for the intensity in the cases $\alpha \le \frac{1}{4}$ and $\alpha > \frac{1}{4}$ gives

$$I(h) = N\delta |f_{\text{ox}}|^2 \left\{ (b_1 - b_2) \frac{1 - [-\frac{1}{2} + (\frac{1}{4}-\alpha)^{1/2}]^2}{1 - 2[-\frac{1}{2} + (\frac{1}{4}-\alpha)^{1/2}]\cos(2\pi h) + [-\frac{1}{2} + (\frac{1}{4}-\alpha)^{1/2}]^2} + (b_1 + b_2) \frac{1 - [-\frac{1}{2} - (\frac{1}{4}-\alpha)^{1/2}]^2}{1 - 2[-\frac{1}{2} - (\frac{1}{4}-\alpha)^{1/2}]\cos(2\pi h) + [-\frac{1}{2} - (\frac{1}{4}-\alpha)^{1/2}]^2} \right\}, \tag{10a}$$

for $\alpha \le \frac{1}{4}$ and $h \neq 0$, $h \neq 1$, and

$$I(h) = N\delta |f_{\text{ox}}|^2 \left\{ b_1'(1-\alpha) \left[\frac{1}{1 + 2\sqrt{\alpha}\cos(2\pi h + \phi) + \alpha} + \frac{1}{1 + 2\sqrt{\alpha}\cos(2\pi h - \phi) + \alpha} \right] - b_2' \sqrt{\alpha} \left[\frac{\sin(2\pi h + \phi)}{1 + 2\sqrt{\alpha}\cos(2\pi h + \phi) + \alpha} - \frac{\sin(2\pi h - \phi)}{1 + 2\sqrt{\alpha}\cos(2\pi h - \phi) + \alpha} \right] \right\}, \tag{10b}$$

for $\alpha > \frac{1}{4}$ and $h \neq 0$, $h \neq 1$. The intensity distributions (10) between the fundamental reciprocal-lattice points describe a diffuse scattering caused by faulting of the regular periodic sequence (2).

Discussion.—The intensity profile associated with a "disordered" distribution of the interstitial defects is given by Eqs. (10). Typical profiles at different stoichiometries are shown in Fig. 1. The calculated profiles have the following important characteristics: (i) If $\alpha = (1-2\delta)/\delta < \frac{1}{4}$ ($\delta \gtrsim 0.444$), Eq. (10a) describes the diffuse maxima at the $(\frac{1}{2}00)$ point. The width of the maximum is of the order of reciprocal average distance between faults. It increases when the stoichiometry deviates from $\delta = 0.5$. (ii) If $\alpha = (1-2\delta)/\delta > \frac{1}{4}$ ($\delta \lesssim 0.444$), the diffraction pattern is described by Eq. (10b). When $\delta < 0.425$, the maximum $(\frac{1}{2}00)$ splits into two maxima $(\frac{1}{2} \pm \epsilon, 0, 0)$ ($h_{\max} = \frac{1}{2} \pm \epsilon$), where ϵ increases with the decrease of δ. The shift of the maxima in the diffraction pattern is described by the plot of $h_{\max}$ vs δ calculated from Eq. (10b) and shown in Fig. 2. It is interesting that the positions of the shifted maxima are very close to the positions $h_{\max} = n/(2n+1)$, for $n = 1, 2, 3$, predicted in Ref. 1 for the superlattice maxima of the completely ordered Magneli phases (compare $h_{\max} = \frac{1}{3}, \frac{2}{5}, \frac{3}{7}$ values with the values $h_{\max} \approx 0.33$, 0.39, 0.47, respectively, following from the plot on Fig. 2).

These calculated results are in agreement with the electron diffraction data of Beyers *et al.*,[9] who actually observed $YBa_2Cu_3O_{7-\delta}$ the diffuse maxima rather than the well-defined superlattice diffraction spots expected for the completely ordered Magneli-type structures. The observed positions of the maxima are close to the $(\frac{1}{2} \pm \epsilon_n, 0, 0)$ positions of the superlattice spots from the nth Magneli phase, where $\epsilon_n = 1/2(2n+1)$, and therefore are close to the positions predicted above for the diffuse maxima (see Fig. 2).

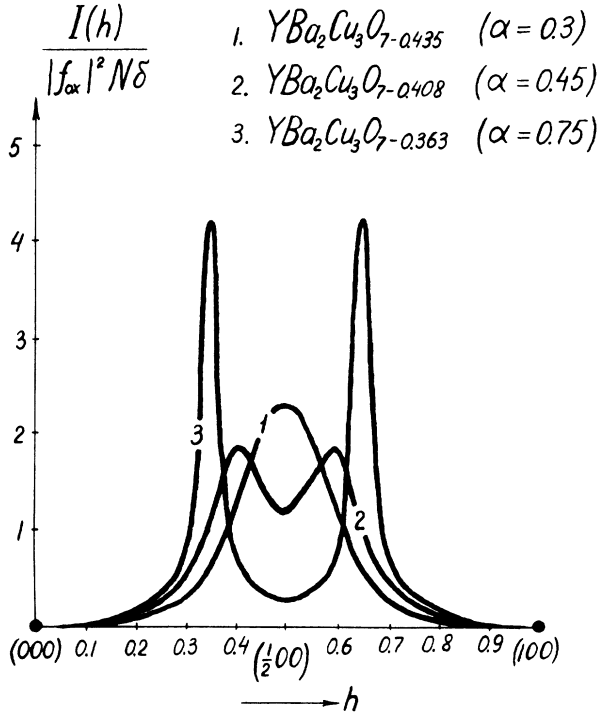

FIG. 1. Calculated intensity profiles associated with random faulting of the ideal double-period $YBa_2Cu_3O_{6.5}$ structure at different stoichiometries: (1) $\delta = 0.435$ ($\alpha = 0.30$), (2) $\delta = 0.408$ ($\alpha = 0.45$), (3) $\delta = 0.363$ ($\alpha = 0.75$).

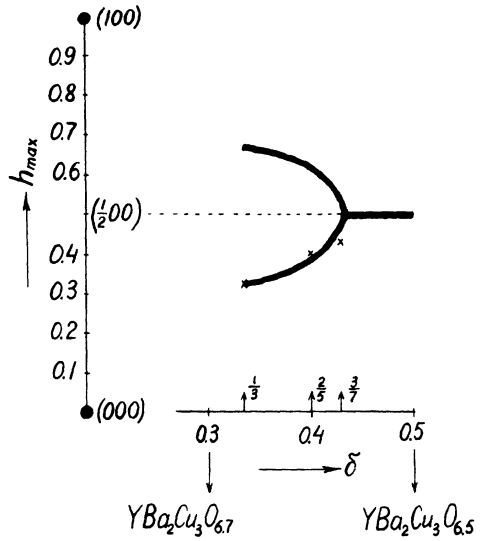

FIG. 2. Calculated positions of the diffuse maxima ($h_{max}00$) caused by the random faulting of the regular double-period structure vs nonstoichiometry parameter, δ.

Equations (10) also predict broadening of the $(\frac{1}{2}00)$-type diffraction maxima when the stoichiometry, δ, deviates from $\delta=0.5$. The broadening is caused by the finite size of the optical coherency domains whose average size is equal to the average distance between faults that break the optical coherency. The typical broadening is then of the order of the reciprocal average distance between faults. The average distance between faults in the relevant model is

$$2a\times\frac{1}{\alpha}=2a\times\frac{\delta}{1-2\delta}.$$

It decreases when the stoichiometry parameter δ deviates from 0.5. Thus, the diffraction maxima become broader. The broadening of the $(\frac{1}{2}00)$-type diffraction maxima caused by deviation of the stoichiometry from $\delta=0.5$ was observed by You, Moodenbaugh, Suenaga, and Tafto.[10] They concluded that the observed broadening is reasonably well described if the assumption is made that the scattering is caused by a set of optically incoherent unit cells of the nth Magneli phase [the size of the cells is equal to the Magneli-phase period $a_n=a(2n+1)$]. The number n was related to the stoichiometry δ through the equation $\delta_n=n/(2n+1)$. It is interesting that this conclusion is actually identical to the conclusions made above for the random faulting model. The agreement between the observed diffraction effects and the predictions of the theory allows us to conclude that *a deviation from the ideal stoichiometry of a primary ordered phase is accommodated not by a change in the occupation of the sublattices but by faulting of the crystal lattice structure caused by the appearance of interstitial plane defects. Nonstoichiometric* $YBa_2Cu_3O_{7-\delta}$ *is then inherently microscopically heterogeneous due to the macroscopic amount of interstitial plane defects induced by the nonstoichiometry.* If this is typical, it may be important for understanding the magnetic pinning properties of the superconducting nonstoichiometric 1:2:3 compound. The faulting mechanism seems to be the main low-temperature mechanism of accommodating the nonstoichiometry not only in $YBa_2Cu_3O_{7-\delta}$ oxides but also in other layer superstructures.

The random faulting model discussed above is applicable within the stoichiometry range of the Magneli homologous structures, $\frac{1}{3}<\delta<\frac{1}{2}$ $(0<\alpha<1)$, where the stoichiometry limits, $\frac{1}{3}$ and $\frac{1}{2}$, are the end values of the Magneli stoichiometry series $\delta_n=n/(2n+1)$ at $n=1$ and ∞, respectively. The results concerning the diffraction effects in the randomly faulted double-period Magneli structure with $n=\infty$ are directly applicable to other Magneli homologous series as well. For example, they are fully applicable to the titanium oxides within the stoichiometry range of the Magneli Ti_nO_{2n-1} series. The random faulting of the routile structure, TiO_2 (it is also a double-period Magneli phase with $n=\infty$) within this range should also result in broadening and shift of the corresponding $(212)_{routile}$ superlattice reflection.

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