Transient Homologous Structures in Nonstoichiometric $YBa_2Cu_3O_{7-x}$

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(Received 22 March 1988)

We propose that a homologous series of transient ordered structures may form during the spinodal decomposition of the nonstoichiometric superconducting oxide $YBa_2Cu_3O_{7-x}$. These transient phases provide the best kinetic accommodation of the local vacancy concentration. Their structures should be similar to those of the Ti_mO_{2m-1} and Mo_mO_{2m-1} series of Magneli phases. The transient phases in the oxide have the stoichiometry $YBa_2Cu_3O_{7-n/(2n+1)}$, where n is an integer. The structure of the n phase has a diffraction maximum at the point $(n/(2n+1)\,0\,0)$. Examples have been experimentally observed.

PACS numbers: 74.70.Vy, 74.70.Sw

In previous work[1,2] we pointed out that the nonstoichiometric compound $YBa_2Cu_3O_{7-x}$ is thermodynamically unstable at low temperature, and used this fact to infer the low-temperature form of the phase diagram as x is varied from 0 to 1. The decomposition terminates in a mixture of the terminal phases $YBa_2Cu_3O_6$ (tetragonal: T) and $YBa_2Cu_3O_7$ (orthorhombic: O). By fitting the calculated thermodynamic values to the available experimental data we obtained the approximate phase diagram that is shown in Fig. 1. The proposed diagram predicts high-temperature decomposition into two orthorhombic phases of different composition followed by low-temperature decomposition into a mixture of T and O, and is at least qualitatively supported by subsequent experimental work.[3-11]

There are, however, indications that the phase-transformation behavior of $YBa_2Cu_3O_{7-x}$ is complicated by the appearance of intermediate ordered states which appear in the form of ultrafine ordered domains.[12-15] These ordered domains do not grow to macroscopic size, and hence appear to be unstable or metastable transient states that occur during low-temperature decomposition.

The appearance of intermediate ordered phases during the decomposition of nonstoichiometric mixed-valence oxides should be a common occurrence. Secondary ordering induced by the repulsion of nonstoichiometric vacancies always reduces the free energy at low temperature and is kinetically favored over decomposition since it is accomplished by short-range atomic rearrangements. Secondary ordering will, therefore, often precede decomposition even if it leads to an end product with a higher thermodynamic potential. If the decomposition is spinodal, as it may be in mixed-valence oxides since charge balance does not constrain the stoichiometry, the decomposition path passes continuously through a range of compositions. Since each composition is compatible with the formation of an ordered phase with an appropriate symmetry and stoichiometry, a homologous series of ordered phases of varying composition may develop. Well-documented examples include TiO_{2-x},[16] VO_{2-x},[17] and MoO_{3-x}.[18] The theory of secondary ordering in these oxides was developed in some detail by one of the present authors.[19,20] It is the purpose of this Letter to describe how this theory may apply to $YBa_2Cu_3O_{7-x}$, to show that it explains the specific ordered states observed in Refs. 13-15, and to discuss some of its implications.

Homologous series of nonstoichiometric oxides. —Prior theoretical work[19,20] addressed the structures of homologous series of nonstoichiometric mixed-valence oxides, and was based on the observation that an ordered phase has the lowest possible free energy if its atomic structure satisfies a "maximum amplitude principle,"

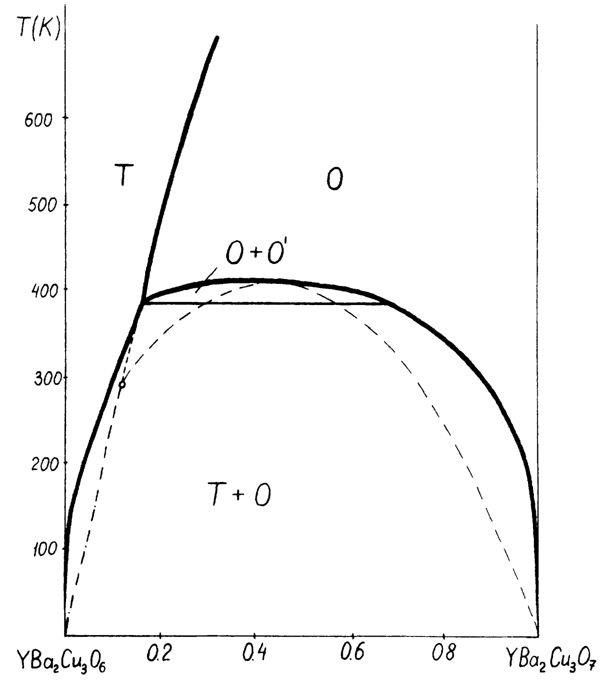

FIG. 1. The predicted equilibrium diagram for $YBa_2Cu_3O_6$-$YBa_2Cu_3O_7$. T=disordered tetragonal phase; O and O' are ordered orthorhombic phases with the same structure but different oxygen content. The dashed line indicates the spinodal curve within the nonstoichiometric O phase.

that is, if the amplitude of the dominant concentration wave that generates the ordered superstructure has the maximum value that is consistent with the given composition. The maximum amplitude requirement is specifically met when atoms and their vacancies form a layer structure composed of alternating filled and vacant planes with periodic faults on every $(2n+1)$th plane. For example, when $n=2$ the layer repeat pattern is $AA\square A\square AA\square A\square$, where A designates a plane of atoms and $\square$ denotes a plane of vacancies. The alternating parallel planes are crystallographic planes of the fully ordered, stoichiometric parent phase that are available for occupancy by nonstoichiometric vacancies. Since the motif of such a structure is $\square_n A_{n+1}$, the concentrations of vacancies, $\square$, and atoms, A are

$$c_v=n/(2n+1),\ \text{and}\ c_A=(n+1)/(2n+1), \tag{1}$$

respectively. The maximum amplitude of the concentration wave generating the nth structure (i.e., the maximum of the diffracted intensity) is associated with the wave vector

$$\mathbf{k}_0=2\pi n\mathbf{H}/(2n+1), \tag{2}$$

where $\mathbf{H}$ is the reciprocal-lattice vector of the parent structure that specifies the alternating plane that generates the structure.

For example, the Ti_mO_{2m-1} Magneli phases in nonstoichiometric TiO_{2-x} rutile have the stoichiometric formula

$$(Ti_{(n+1)/(2n+1)}\square_{n/(2n+1)})O,$$

where $m=n+1$ is a series of integers that characterize the members of the series. Similar structures occur in the V_mO_{2m-1} oxides. For these structures the maximum-intensity diffraction spots are given by the maximum-amplitude principle and fall on the generic

$$\frac{n}{2n+1}(121)=\frac{m-1}{2m-1}(121)$$

reciprocal-lattice points in the rutile structure, where (121) is the index of the alternating plane. Secondary ordering in nonstoichiometric MoO_{3-x} oxides results in the Magneli homologous series with the stoichiometric formula

$$(Mo_{(n+1)/(2n+1)}\square_{n/(2n+1)})(O_{(n+1)/(2n+1)}\square_{n/(2n+1)})O,$$

or Mo_mO_{3m-1}, where $m=n+1$.[20] The homologous series $(Mo,W)_mO_{3m-1}$ for $8\leq m\leq 14$ is generated by the dominant concentration wave related to the maximum intensity spot at $[(m-1)/(2m-1)](420)$; (420) is the alternating plane.[21]

Possible Magneli-type structures in $YBa_2Cu_3O_{7-x}$.—A similar structural behavior may be expected in orthorhombic $YBa_2Cu_3O_{7-x}$. The chemical formula of the oxide can be written $YBa_2Cu_3O_6(O_{1-x}\square_x)$ where the parenthetical expression describes the fractions of oxygen atoms and vacancies in the (001) basal plane of the $YBa_2Cu_3O_7$ structure. If a Magneli-type homologous series is formed, the structures and stoichiometries of its members should be determined by the maximum-amplitude principle. According to Eq. (1) the stoichiometric formulas should be

$$YBa_2Cu_3O_6(O_{(n+1)/(2n+1)})=YBa_2Cu_3O_{7-n/(2n+1)}. \tag{3}$$

The maximal intensity superlattice reflections should fall at the reciprocal-lattice sites specified by Eq. (2), where $\mathbf{H}$ is the reciprocal-lattice vector of the parent $YBa_2Cu_3O_7$ oxide that corresponds to the alternating crystal lattice planes of vacancies and oxygen atoms. Substituting the integer series $n=1,2,3\ldots$ into Eq. (3) we obtain the possible homologous series of the transient secondary ordered oxides:

$$\begin{gathered}YBa_2Cu_3O_{7-1/3},\ YBa_2Cu_3O_{7-2/5},\\ YBa_2Cu_3O_{7-3/7},\ \ldots,\ YBa_2Cu_3O_{7-1/2}.\end{gathered} \tag{4}$$

The members of this homologous series are not equally stable. Some may appear only at particular values of the temperature and composition; others may not appear at all.

It follows from Eq. (2) that the superlattice reflections related to the dominant (maximum amplitude) concentration wave are $\frac{1}{3}\mathbf{H}$, $\frac{2}{5}\mathbf{H}$, $\frac{3}{7}\mathbf{H},\ldots,\frac{1}{2}\mathbf{H}$. If the homologous phases are formed by the alternation of filled and vacant (100) planes in the $YBa_2Cu_3O_7$ structure, i.e., $\mathbf{H}=\mathbf{H}_{(100)}$, then the maximum-intensity superlattice diffraction maxima for the homologous phases are $(\frac{1}{3}00)$ $[YBa_2Cu_3O_{7-1/3}]$, $(\frac{2}{5}00)$ $[YBa_2Cu_3O_{7-2/5}]$, $(\frac{3}{7}00)$ $[YBa_2Cu_3O_{7-3/7}],\ldots,(\frac{1}{2}00)$ $[YBa_2Cu_3O_{7-1/2}]$. The associated diffraction pattern is shown schematically in Fig. 2. These phases are all orthorhombic, but have orthorhombicity ratios that decrease with n.

The structural observations that have recently been reported on secondary ordering in orthorhombic $YBa_2Cu_3O_{7-x}$ are in at least qualitative agreement with the predictions of the theory. The observed superlattice diffraction spots can be attributed to the appearance of a transient Magneli-type homologous series $YBa_2Cu_3O_{7-n/(2n+1)}$ during decomposition. Diffraction maxima at $(\frac{1}{3}00)$ $(n=1)$ were observed by Chen *et al.*[14]; the corresponding tripling of the period along the $[100]$ direction was imaged by Van Tendeloo *et al.*[13] Werder *et al.*[15] found $(\frac{2}{5}00)$ diffraction maxima $(n=2)$. They also observed diffuse maxima at $(\frac{1}{2}00)$, whose source may either be the limiting structure at $n=\infty$, or the accumulation of diffraction intensity from structures with high values of n. The $(\frac{2}{5}00)$ maxima were seen only when the composition of the $YBa_2Cu_3O_{7-x}$ lay within the range $0.3<x<0.4$, in good agreement with the predicted stoichiometry $x=\frac{2}{5}$ of the $YBa_2Cu_3O_{7-2/5}$

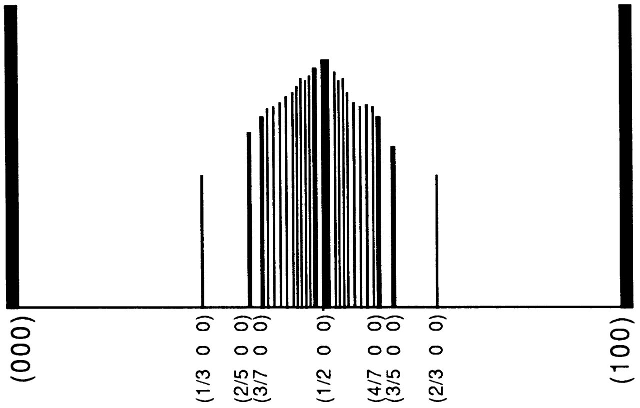

FIG. 2. Schematic diffraction pattern of the transient $YBa_2Cu_3O_{7-n/(2n+1)}$ structures.

homologous phase.

The status of the other members of the homologous series at $n=3,\ldots,\infty$ is not clear yet. They were not observed either because they did not form or because when $n \geq 3$ the positions of the relevant diffraction maxima lie so close to one another and to the maximum at $(\frac{1}{2}00)$ that they are not resolved, but are rather gathered into the broad, diffuse maximum around $(\frac{1}{2}00)$ (Fig. 2).

The $(n/(2n+1)00)$ homologous phases [including the $(\frac{1}{2}00)$ phase] were found only in the form of ultrafine domains that did not grow to macroscopic size. This observation suggests that the homologous structures are transient unstable or metastable states along the decomposition path. If so, the behavior of the oxide resembles that of Ni-Mo and Au-Pt alloys, in which $(1\frac{1}{2}0)$ maxima that never develop into conventional superstructures are also observed.[22,23]

To construct the homologous structures of $YBa_2Cu_3O_{7-x}$ the nonstoichiometric vacancies, □, should be distributed in an ordered pattern over the regular O-atom sites in the (001) basal planes of the ordered $YBa_2Cu_3O_7$ structure with a fault on each nth plane (Fig. 3). The [010] lines filled by O atoms and their vacancies alternate in the pattern OO□OO□ for the $x=\frac{1}{3}$ structure [Fig. 3(b)], OO□O□OO□O□OO for $x=\frac{2}{5}$ [Fig. 3(c)], and O□O□O□ for $x=\frac{1}{2}$ [Fig. 3(d)].

Now consider the transformation path of $YBa_2Cu_3O_{7-x}$ when it is cooled to a temperature below the secondary spinodal shown by the dashed line in Fig. 1. The supercooled, nonstoichiometric phase preferentially decomposes into two orthorhombic phases by the spinodal mechanism (a similar type of secondary decomposition within the ordered phase occurs in cubic Al-Li[24] and Fe-Al[25] alloys). The oxygen content of one of the decomposition products evolves towards $YBa_2Cu_3O_7$ (x decreases) while the oxygen content of the other evolves towards the $YBa_2Cu_3O_6$ (x increases). During this decomposition the oxygen contents of the decomposing phases pass sequentially through the series of stoichiometric compositions of the Magneli-type phases at $x=n/(2n+1)$. Since the overall oxygen content of a macroscopic phase, which is controlled by bulk diffusion, evolves slowly compared to the relaxation time for secondary ordering, which requires only local atom jumps, the formation of a transient homologous phase is kinetically favored whenever it is thermodynamically preferred to the parent orthorhombic phase at the local value of the composition. Given the spatial variation in mean composition during spinodal decomposition, the homologous phase is not expected to grow to macroscopic size before the evolution of the local composition shifts to the next homologous phase in the series. The reduction of the oxygen content in the oxygen-lean O phase during the decomposition reaction should continue until it reaches the limit of stability with respect to disorder. At that point the oxygen-lean orthorhombic phase spontaneously disorders to create the equilibrium, tetragonal $YBa_2Cu_3O_6$.

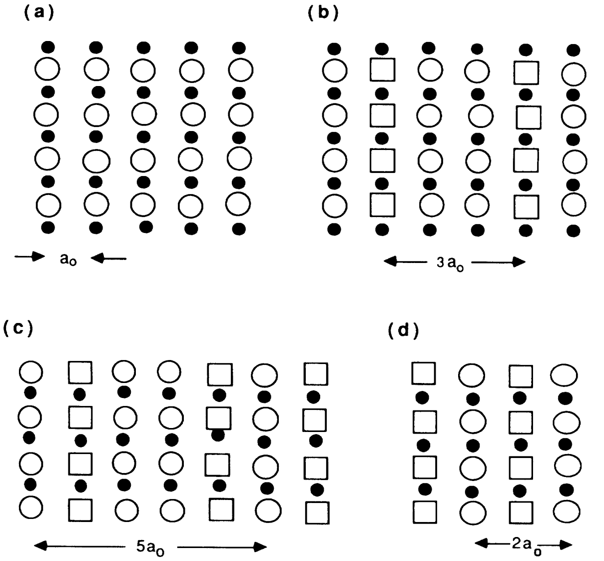

FIG. 3. The distribution of atoms and vacancies in the basal plane in the ordered, homologous structures $YBa_2Cu_3O_{7-n/(2n+1)}$. (a) $YBa_2Cu_3O_7$, (b) $YBa_2Cu_3O_{7-1/3}$, (c) $YBa_2Cu_3O_{7-2/5}$, (d) $YBa_2Cu_3O_{7-1/2}$.

The kinetic competition between rates of decomposition and ordering may explain the very interesting results of recent high-resolution x-ray synchrotron radiation studies of single crystals of $YBa_2Cu_3O_{7-x}$.[6] The authors of Ref. 6 concluded from the observed splitting of (110) twins that $YBa_2Cu_3O_{7-x}$ may simultaneously contain three or more orthorhombic phases with a fine-scale phase separation. A similar phenomenon was observed in another superconducting oxide $(La_{1.8}Ba_{0.2})CuO_{4-x}$.[26] This phenomenon cannot be explained by spinodal decomposition alone since the continuous spatial variation of composition in the spinodal would lead to a continuous spectrum in the (110) twin-splitting diagram.

According to the diagram shown in Fig. 1, the oxide decomposes at room temperature when its oxygen content falls below the $YBa_2Cu_3O_{6.8}$ stoichiometry (this solubility limit has been confirmed by Raman scattering data[9,10]). If the decomposition results in the formation of fine-scale domains of the homologous structures it may be responsible for the drop in T_c from 90 to 60 K that is observed below this composition.

Finally, note that this discussion treated oxides with $x \leq 0.5$, which have a homologous series that terminates in the $(\frac{1}{2}00)$ phase $(n=\infty)$ with the composition $YBa_2Cu_3O_{6.5}$. While a "mirror-image" series with $x > 0.5$ is possible, its stability is questionable because of the high vacancy concentration. When $x > 0.5$ we would expect direct decomposition into a two-phase mixture of T and O.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

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[1] A. G. Khachaturyan and J. W. Morris, Jr., Phys. Rev. Lett. **59**, 2776 (1987).

[2] A. G. Khachaturyan, S. V. Semenovskaya, and J. W. Morris, Jr., Phys. Rev. B **37**, 2243 (1988).

[3] D. G. Hinks, B. Dabrowski, M. A. Beno, L. Soderholm, I. K. Schuller, C. V. Segre, and K. Zhang, unpublished.

[4] J. Brynstad, E. D. Specht, C. J. Spark, A. G. Dhere, O. B. Cabin, D. M. Kroeger, R. K. Williams, H. E. Oye, and J. F. Seiler, unpublished.

[5] M. Eibschutz, M. E. Lines, J. M. Tarascon, and P. Barboux, Phys. Rev. B (to be published).

[6] H. You, J. D. Axe, X. B. Kan, S. C. Moss, J. F. Liu, and D. J. Lam, Phys. Rev. B **37**, 2301 (1988).

[7] D. S. Lee, Z. Fu, W. L. Johnson, P. Pietrovski, and K. Samwer, unpublished.

[8] M. Sarikaya and E. A. Stern, unpublished.

[9] M. S. Zhang, C. Qiuang, S. Dakun, R. Ji, Z. Qin, Y. Zheng, and J. F. Scott, Solid State Commun. **65**, 987 (1988).

[10] J. F. Scott, M. S. Zhang, and Y. Wang, Bull. Am. Phys. Soc. **33**, 539 (1988).

[11] G. Burns, F. H. Dacob, F. Holtzberg, and D. L. Kaizer, Solid State Commun. **66**, 217 (1988).

[12] C. H. Chen, D. J. Werder, L. F. Schneemeyer, P. K. Gallagher, and J. V. Waszczak, Phys. Rev. B (to be published).

[13] G. Van Tendeloo, H. W. Zandbergen, and S. Amelinckx, Solid State Commun. **63**, 289, 606 (1987).

[14] C. H. Chen, D. J. Werder, R. J. Cava, L. F. Schneemeyer, B. Batlogg, and P. K. Gallagher, unpublished.

[15] D. I. Werder, C. H. Chen, R. J. Cava, and B. Battlogg, Phys. Rev. B **37**, 2318 (1988).

[16] S. Andersson, B. Collen, V. Kuylenstierna, and A. Magneli, Acta Chem. Scand. **11**, 1641 (1957).

[17] G. Anderson, Acta Chem. Scand. **8**, 1599 (1954).

[18] A. Magneli, Acta Chem. Scand. **2**, 501 (1948).

[19] B. I. Pokrovskii and A. G. Khachaturyan, J. Solid State Chem. **61**, 154 (1986).

[20] A. G. Khachaturyan and B. I. Pokrovskii, in *Progress in Materials Science,* edited by J. W. Christian, P. Haasen, and T. Massalski (Pergamon, Oxford, 1985) Vol. 29, pp. 1–138.

[21] R. Collongues, *La Non-Stoechiometrie* (Mason, Paris, 1971).

[22] M. Yamamoto, N. Soji, T. Sabury, and J. Mitutani, Trans. Jpn. Inst. Met. **11**, 120 (1970).

[23] S. K. Das, P. R. Okomota, D. H. J. Fischer, and G. Thomas, Acta Metall. **21**, 913 (1973).

[24] A. G. Khachaturyan, T. F. Lindsey, and J. W. Morris, Jr., Metall. Trans. **19A**, 249 (1988).

[25] S. V. Semenovskaya, Phys. Status Solidi B **64**, 291 (1974).

[26] S. C. Moss, K. Foster, J. D. Axe, H. You, D. Hohlwein, D. E. Cox, R. L. Meng, P. H. Hon, and C. W. Chu, Phys. Rev. B **35**, 7195 (1987).