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Mendeleev Commun., 1991, **1(2)**, 65–67

Mendeleev Communications

Thermodynamic Stability of Superconductors $Y_2Ba_4Cu_{6+n}O_{14+n}$ ($n = 0, 1, 2, \ldots$)

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Stability fields of superconductors in the Y–Ba–Cu–O system have been obtained.

The thermodynamic stability of superconductors is of both theoretical and practical interest. It is important to confirm or refute the wide-spread point of view, that superconductors are always thermodynamically unstable.[1] This supposition is derived from the general idea that a strong atomic disordering must take place in a superconducting crystal. If such a rule were substantiated, it could be used as a guide for the synthesis of new superconducting substances.

On the other hand, stability fields of existing superconductors are of practical importance because new technologies may be developed for the production of superior materials based on such thermodynamic data.

We have considered the well-known solid solution $YBa_2Cu_3O_{6+z}$, where $0 \leqslant z \leqslant 1$, which is often denoted '123' for brevity, and several new superconductors from the family of phases $Y_2Ba_4Cu_{6+n}O_{14+n}$. Two of them, $YBa_2Cu_4O_8$ ('124') and $Y_2Ba_4Cu_7O_{14+z}$ ('247'), were obtained this year in bulk form under 1 atm oxygen pressure. The next phase, '125', from that homologous series has already been obtained in films and most likely will be synthesized in bulk too.[2–4]

All the phases under consideration have common structural patterns $YBa_2Cu_2O_6$ divided by one or several —CuO_z— layers. In the case of a single layer, the oxygen composition may vary in the range $0 \leqslant z \leqslant 1$, so the phase is a solid solution. If there are two or three layers between the $YBa_2Cu_2O_6$ patterns, the corresponding phase has approximately constant stoichiometry with $z = 1$. Based on these structural data, thermodynamic models of the superconductors were devised.

The dependence of the thermodynamic properties of the solid solutions on the oxygen composition and also the second order orthorhombic-to-tetragonal phase transition was described by consideration of the formation and ordering of the oxygen vacancies in the —CuO_z— planes.[8] This model describes simultaneously the thermodynamic and structural properties of the '123' and '247' solid solutions and also those of the other phases containing the single —CuO_z— layers. The parameters of the model were fitted to the following experimental data: neutron diffraction[9] and X-ray diffraction[10] studies of the oxygen occupancies of different sites in the —CuO_z— plane, data on the orthorhombic-to-tetragonal phase transition curve,[9–16] the equilibrium oxygen partial pressure obtained as a function of composition and temperature,[11–13,17–22] calorimetric measurements of the specific heat[23–29] and partial enthalpy of oxygen,[12,30] and the integral Gibbs energy obtained by an EMF method.[31–33] More than 600 experimental data points from 25 publications were used, compiled by using a specially devised optimization program.

The thermodynamic functions of formation of the '123' phase according to the reaction $1/2\,Y_2O_3 + 2BaO + 3CuO + (z-0.5)/2O_2 \rightarrow YBa_2Cu_3O_{6+z}$ for temperatures above 100 K and compositions $0 \leqslant z \leqslant 1$ are given in eqns. (1)–(4), where x is

$$\Delta_f G^{ox}(YBa_2Cu_3O_{6+z}, T, z, x) = \Delta_f H^{ox} - T\Delta_f S^{ox} \quad (1)$$

$$\Delta_f H^{ox}/R = A_1 + A_2 z + z(1-z)a_1^h + (c^2 - x^2)b_1^h - \Delta_r H^\circ/R \quad (2)$$

$$\Delta_f S^{ox}/R = B_1 + B_2 z + z(1-z)[a_1^s + a_2^s(1-z)] + (c^2 - x^2)b_1^s + S^{id}/R - \Delta_r S^\circ/R \quad (3)$$

$$S^{id}/R = -(c+x)\ln(c+x) - (c-x)\ln(c-x) - (1-c+x)\ln(1-c+x) - (1-c-x)\ln(1-c-x) - z\ln z - (1-z)\ln(1-z) \quad (4)$$

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the order parameter which depends on the oxygen ordering in the —CuO_z—planes (for the tetragonal phase $x = 0$, and for the completely ordered orthorhombic phase $x = c$); $c = z/2$; $R = 8.314$ J mol^{-1} K^{-1}; $A_1 = -13475$ K; $B_1 = -2.543$; $A_2 = -10669.8$ K; $B_2 = -10.4058$; $a_1^h = 886.731$ K; $a_p^s = 0.4871$; $a_2^s = -1.4204$; $b_1^h = 1158.53$ K; $b_1^s = -3.33514$. The standard functions $\Delta_r H^\circ$ and $\Delta_r S^\circ$ correspond to the reaction $1/2Cu_2O + 1/4O_2 \rightarrow CuO$. The equilibrium values of the order parameter x, oxygen content z, and oxygen pressure $P(O_2)$ are interrelated by equations (5) and (6).

$$T\ln[(c + x)(1 - c + x)/(c - x)/(1 - c - x)] = 2(b_1^h - Tb_1^s)x \quad (5)$$

$$\ln P(O_2) = \ln\{(c + x)(c - x)z^2/[(1 - c - x)(1 - c + x)(1 - z)^2]\} + 2[A_2 - TB_2 + (a_1^h - Ta_1^s)(1 - 2z) - Ta_2^s(1 - z)(1 - 3z) + c(b_1^h - Tb_1^s)]/T \quad (6)$$

The thermodynamic functions of the '247' solid solution are described by the same formulae, with the terms $\Delta_r H^\circ$ and $\Delta_r S^\circ$ doubled and the parameters A_1 and B_1 replaced by $A_1^{247} = -39699$ K and $B_1^{247} = -15.492$. The thermodynamic properties of all the other phases in the Y–Ba–Cu–O system are necessary for the calculations. They were assessed based on experimental data available in the literature.

The phase equilibria and the stability field of the '123' solid solution are shown in Fig. 1. The '123' is thermodynamically stable only in the cross-hatched field limited by the bold lines, which correspond to an equilibrium of four solid phases and a gas. At temperatures and compositions outside this field, the '123' is thermodynamically unstable and decomposes into other substances in the Y–Ba–Cu–O system according to the reactions mentioned in the Fig. 1 caption. However, when the nucleation and growth of phases with cation stoichiometry other than '123' are kinetically prohibited, the '123' phase may exist for a long time as a metastable phase. In such a case, the metastable equilibria between the orthorhombic and tetragonal phases represented by the dotted lines in Fig. 1 take place. The equilibrium oxygen composition of the '123' varies with temperature and oxygen pressure. Some isobars are shown in Fig. 1.

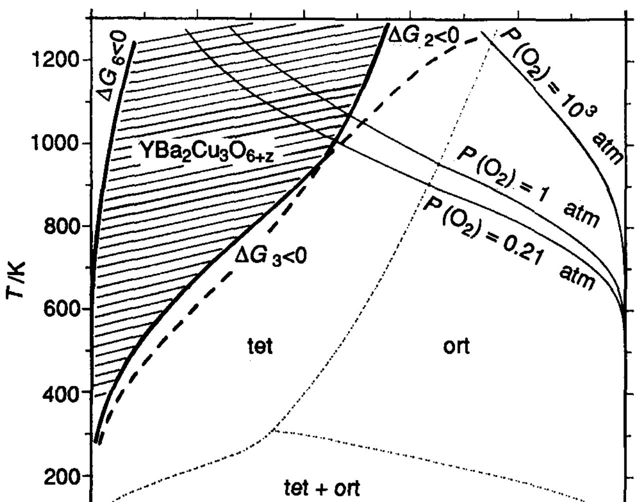

Fig. 1 Stability field of the '123' phase. Thin solid lines represent temperature dependence of equilibrium composition at fixed oxygen pressure. Bold solid lines represent decomposition according to reactions (2), (3) and (6).

$$6YBa_2Cu_3O_{6+z} \rightarrow Y_2BaCuO_5 + 3BaCuO_{2.35} + 2Y_2Ba_4Cu_7O_{14+z} + (4z - 4.05)/2\ O_2 \quad (2)$$

$$6YBa_2Cu_3O_{6+z} \rightarrow Y_2BaCuO_5 + 3BaCuO_2 + 2Y_2Ba_4Cu_7O_{14+z} + (4z - 3)/2\ O_2 \quad (3)$$

$$9YBa_2Cu_3O_{6+z} \rightarrow 4Y_2BaCuO_5 + YBa_4Cu_3O_{8.5} + 10BaCu_2O_2 + (5.5 + 9z)/2\ O_2 \quad (6)$$

Dotted lines represent equilibria of orthorhombic and tetragonal phases.

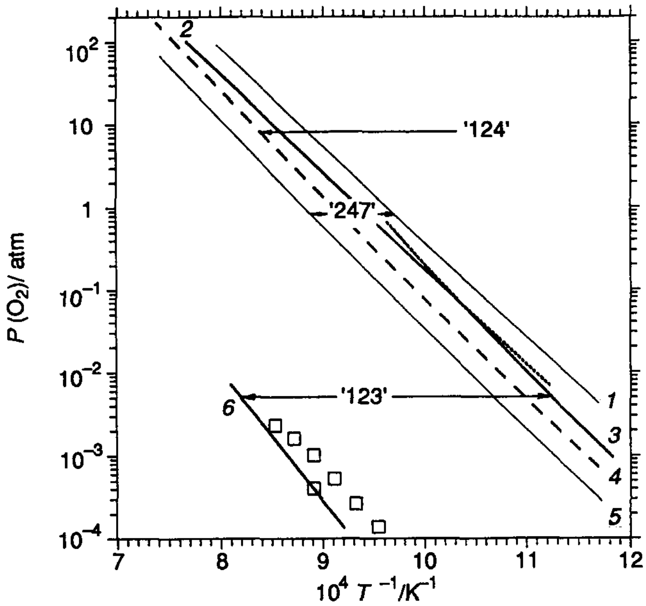

Fig. 2 Stability fields of superconducting phases in the Y–Ba–Cu–O system. Bold solid lines represent decomposition of the '123' phase, while thin solid lines represent decomposition of the '247' phase according to reactions (1) and (5).

$$4Y_2Ba_4Cu_7O_{14+z} \rightarrow Y_2BaCuO_5 + 6YBa_2Cu_4O_8 + 3BaCuO_{2.35} + (4z - 4.05)/2\ O_2 \quad (1)$$

$$Y_2Ba_4Cu_7O_{14+z} \rightarrow 2YBa_2Cu_3O_{6+z} + CuO + (1 - z)/2\ O_2 \quad (5)$$

Dashed line represents decomposition of the '124' phase according to reaction (4).

$$2YBa_2Cu_4O_8 \rightarrow Y_2Ba_4Cu_7O_{14+z} + CuO + (1 - z)/2\ O_2 \quad (4)$$

(□): experimental data of Ahn *et al.*[5,6]

Evidently, the superconducting orthorhombic phase is thermodynamically unstable at any temperature and composition. Hence a two-stage method is generally used to obtain it in a metastable state. The tetragonal phase is first synthesized at 900–960 °C and at oxygen pressure 0.2–1 atm, which correspond to the region of its stability shown in Fig. 1. The superconducting orthorhombic structure is then prepared and annealed to increase the oxygen stoichiometry by equilibrating the tetragonal phase under 1 atm oxygen pressure at lower temperatures in accordance with the metastable equilibria of the orthorhombic and tetragonal phases (see dotted lines and 1 atm isobar in Fig. 1).

Phase boundaries corresponding to different decomposition reactions are often close to each other. Owing to the experimental uncertainties in the values of the thermodynamic properties of the phases used for the calculations, it is hard to indicate which of these boundaries is stable and which is metastable, although the stability field remains practically unchanged. For example, line *6* in Fig. 1 and the phase boundary for the decomposition of the '123' into Y_2BaCuO_5, $BaCuO_2$, $BaCu_2O_2$, and O_2 are almost coincident and describe rather well the experimental data of Ahn *et al.*[5,6] Furthermore, calculations were made under the assumption that there are two phases of barium cuprate, namely $BaCuO_2$ and $BaCuO_{2.35}$, as proposed by Scolis *et al.*[7] It is possible to interpret his results in terms of the existence of only one phase $BaCuO_{2+y}$ with a wide homogeneity range. In this case, there is only one continuous curve in Fig. 1 instead of lines *2* and *3*, but the stability field is not changed markedly.

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The stability fields of the superconducting phases, which were synthesized in the Y–Ba–Cu–O system, are presented in Fig. 2. When the corresponding cation composition is fixed, the '123' is stable between lines *2*, *3* and *6*, the '247' between *1* and *5* and the '124' above line *4*. Evidently, at low temperature and moderate oxygen pressure only the '124' phase is stable, so this is the only superconductor which is thermodynamically stable in conventional application conditions. It should be noted that the '124' phase may appear to be unstable to decomposition into other phases from homologous series $Y_2Ba_4Cu_{6+n}O_{14+n}$ such as the '125'. The latter must be stable at higher oxygen pressures and is probably a superconductor also. Fig. 2 may be used as a guide for the synthesis of the '123', '124' and '247' superconductors.

Received in USSR, 20th November 1990
Received in UK, 25th January 1991; *Com. 0/05338D*

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