

**Theory for oxygen content and ordering in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  in equilibrium with oxygen gas**

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A model using statistical thermodynamics is presented which quantitatively describes the oxygen content and ordering in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ . This model is in good agreement with experiments within a broad range of temperature and oxygen partial pressure. In the framework of this model it is found that the site (binding) energy of the oxygen in the lattice is quadratic in the oxygen concentration and linear in the temperature. A possible relation of this dependence to the electronic structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  is discussed.

The oxygen content and its distribution (ordering) among the atomic sites strongly affect the value of the transition temperature to superconductivity  $T_c$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ .<sup>1</sup> It is for this reason that the oxygen- $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  system has been the subject of many experimental<sup>2-7</sup> and theoretical<sup>4,7-11</sup> studies. *In situ* neutron-diffraction experiments, in which equilibrium fractional site occupancies of oxygen are determined have been indispensable to these studies.<sup>4,8,9,11</sup> In this Rapid Communication we report the results of a thermodynamical analysis of the most recent *in situ* neutron-diffraction experiment.<sup>12</sup> In this analysis, the dependence of the heat of solution of oxygen in the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  lattice on the oxygen concentration in the lattice and the lattice temperature is determined. This determination leads to a quadratic dependence of the site (binding) energy on concentration and linear dependence on temperature. Previous similar analyses of *in situ* neutron-diffraction results have shown<sup>8,9</sup> a linear dependence of the site energy on concentration only. Possible physical mechanisms which may lead to this quadratic dependence will be discussed.

The structure of  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  can be represented<sup>13</sup> (at  $x=1$ ) by stacking layers of CuO, BaO, CuO<sub>2</sub>, Y, CuO<sub>2</sub>, BaO, CuO, . . . , along the  $c$  axis. The oxygen adsorption and desorption takes place mostly (but not exclusively<sup>12</sup>) in the CuO planes (Fig. 1). The CuO plane

has two oxygen sites  $\alpha$  and  $\beta$  which correspond to O(5) and O(1) (Ref. 2), respectively. As  $x$  approaches 1, the  $\alpha$  site is nearly vacant ( $c_\alpha=0$ ), the  $\beta$  site is nearly fully occupied ( $c_\beta=1$ ), and  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$  is in its orthorhombic ( $Pmmm$ ) phase.<sup>13</sup> *In situ* neutron-diffraction experiments show<sup>3,12</sup> that as temperature is increased and/or oxygen partial pressure is decreased oxygen adsorption and desorption take place at the  $\alpha$  and  $\beta$  sites, respectively. This process continues until a critical temperature  $T_{OT}$  and pressure  $P_{OT}$  are reached, at which  $c_\alpha=c_\beta$ , and the structure transforms from orthorhombic to tetragonal ( $P/4mmm$ ).

In an attempt to reproduce this behavior by calculations, we shall use, following previous work,<sup>8,9,14</sup> the quasichemical approximation (QCA) (also known as Fowler-Guggenheim method or the pair approximation). In this model it is assumed that the oxygen adsorption and desorption take place exclusively at the CuO plane, which is treated as a two-dimensional lattice gas. The heat of solution of the oxygen atom (initially in the molecular state) is  $E$  (eV) and the nearest-neighbor (NN) repulsion between oxygen on  $\alpha$  and oxygen on  $\beta$  is  $V$  (eV). Short-range order is introduced using fractional site occupancy for oxygen ( $\alpha$ )-oxygen ( $\beta$ ) NN pairs,  $q = N_{\alpha\beta}/4N$  [ $N_{\alpha\beta}$  is the number of oxygen NN  $\alpha$ - $\beta$  pairs,  $4N$  is the number of pair sites where  $N$  is the total number of oxygen ( $\alpha$  and  $\beta$ ) sites in the CuO plane (Fig. 1)]. We also introduce oxygen concentration in the CuO plane  $c$  and order parameter  $s$  which are related to the fractional site occupancies  $c_\alpha$  and  $c_\beta$  as follows:

$$c = (c_\beta + c_\alpha)/2, \quad s = (c_\beta - c_\alpha)/(c_\beta + c_\alpha),$$

or (1)

$$c_\alpha = c(1 - s), \quad c_\beta = c(1 + s).$$

We shall now follow the standard treatment of statistical thermodynamics.<sup>14</sup> Equating the chemical potential of an oxygen atom in the lattice gas to that of the oxygen atom in the molecular gas yields<sup>8</sup>

$$\ln \left[ \left( \frac{1 - c(1 + s)}{c(1 + s)} \right)^3 \left( \frac{c(1 + s) - q}{1 - 2c + q} \right)^4 \right] = -\ln \left[ \frac{PT^{-7/2}}{3(1 - e^{-2230/T})} \right]^{1/2} - \frac{E}{kT}. \quad (2)$$

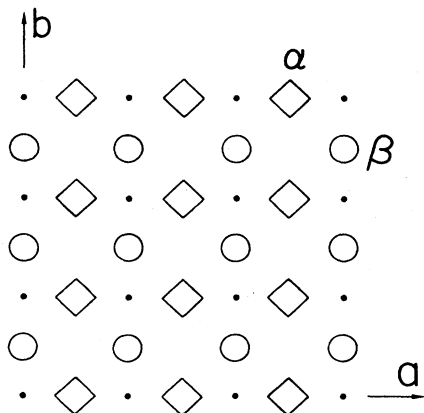


FIG. 1. The CuO plane. Copper sublattice, Cu(1) site (dots); oxygen  $\alpha$  sublattice, O(5) site (squares); oxygen  $\beta$  sublattice O(1) site (circles).

Minimizing the free energy with respect to  $q$  and  $s$  yields the following two equations:<sup>8,14</sup>

$$\ln \frac{[c(1+s)-q][c(1-s)-q]}{q(1-2c+q)} = \frac{V}{kT}, \quad (3)$$

$$\ln \frac{c(1+s)-q}{c(1-s)-q} = \frac{3}{4} \ln \frac{(1+s)[1-c(1-s)]}{(1-s)[1-c(1+s)]}. \quad (4)$$

We first point out that  $q$  is completely determined by  $c$  and  $s$  through a single equation [Eq. (4)]. Hence the mathematical problem reduces to simultaneously solving Eqs. (2) and (3) for  $c$  and  $s$ . These equations operate in the space  $(V, E, T, P, c, s)$ . For example, given  $(V, E, T, P)$   $c$  and  $s$  are (apart from a solution  $c, s = 0$  which always exists) uniquely determined. Conversely, given  $M$  sets of  $(T_i, P_i, c_i, s_i)$  which were determined in neutron-diffraction

experiments,  $V$  and  $E$  can be refined to give  $c$  and  $s$  values that best fit the experimental values  $c_i$  and  $s_i$  at each  $(T_i, P_i)$ .

Previous studies of the model described above have shown<sup>8,9</sup> that  $V$  is a constant at about 0.2 eV, whereas,  $E$  was found to be concentration dependent. In order to separate the  $c$  dependence from a possible  $T$  dependence of  $E$ , we first refined  $E$  with respect to two *in situ* isothermal neutron-diffraction experiments<sup>12</sup> at  $(490, P)$  and  $(440, P)$  [the first and second entries designate temperature ( $^{\circ}C$ ) and oxygen partial pressure (atmospheres), respectively]. This refinement yielded (for the orthorhombic phase) a quadratic  $c$  dependence of  $E$ . As the refinement was extended to include a third *in situ* isobaric neutron-diffraction experiment<sup>2</sup> at  $(T, 1)$  it yielded (see Fig. 2):

$$E = -0.818 - 0.307T/1000 + \begin{cases} 5.91(c-0.25)^2 & \text{orthorhombic,} \\ 0 & \text{tetragonal.} \end{cases} \quad (5)$$

The site occupancies which were calculated using the QCA with  $V=0.2$  eV and  $E$  as given by Eq. (5) are plotted (solid line) in Fig. 3 with the experimental occupancies (circles). The latter were obtained by fitting the calculated to the observed<sup>2,12</sup> neutron-diffraction intensities (Rietveld refinement). In the previous studies, the values  $E = -1.17$  eV (Ref. 8) and  $E = -1.56 + 1.5c$  (Ref. 9) were found to fit the  $(T, 1 \text{ atm})$  run leading to an orthorhombic-to-tetragonal transition at  $T=700^{\circ}C$  and  $c=0.25$ . Near this transition, Eq. (5) yields  $E = -1.17$  eV in agreement with the results of the previous studies. In the  $(440, P)$  and  $(490, P)$  runs, on the other hand, the results of the previous studies are in disagreement with Eq. (5) and are therefore incapable of fitting the data.

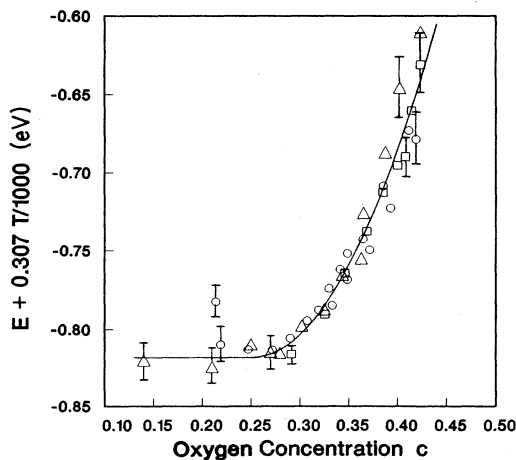


FIG. 2. The temperature and concentration dependence of the heat of solution  $E$ , of oxygen in  $YBa_2Cu_3O_{6+x}$ . Values of  $E$  were calculated in the QCA using the observed site occupancies. Squares, circles and triangles correspond to the  $(440, P)$ ,  $(490, P)$ , and  $(T, 1)$  experiments. The solid line represents the best fit to these results [Eq. (5)].

To calculate the orthorhombic-to-tetragonal (OT) transition in the QCA, Eqs. (2), (3), and (4) are simultaneously taken to the limit  $s \rightarrow 0$ . This yields

$$\ln \left[ \left( \frac{1-c}{c} \right)^3 \left( \frac{c}{0.75-c} \right) \right]^4 = \ln \left[ \frac{PT^{-7/2}}{3(1-e^{-2230/T})} \right]^{1/2} - \frac{E}{kT}, \quad (6)$$

$$\ln \frac{16c(1-c)}{1-4(1-2c)^2} = \frac{V}{kT}, \quad (7)$$

$$(4c-1)c/3 = q. \quad (8)$$

These equations define the OT transition line in  $(T, P, c)$  space. The projection on to the  $T$ - $P$  plane of the OT transition line predicted by the QCA [i.e., Eqs. (5)–(8)] is shown (solid line) in Fig. 4. OT transition points which were determined experimentally by *in situ* neutron-diffraction (circles),<sup>2,12</sup> resistivity measurements (squares),<sup>3</sup> and thermogravimetry (triangles)<sup>4</sup> are also shown. The results of the three experimental techniques are (except for a pair of neutron diffraction points) in good agreement with each other. Hence, the OT transition line predicted by the QCA is in good agreement with experiments. The discrepancy with the two OT transition points reported<sup>2</sup> for the isobaric *in situ* experiments at  $(T, 0.2)$  and  $(T, 0.02)$  is not clear to us at this stage. It is suggested that inappropriate equilibration time and perhaps some leaks in the oxygen system are responsible for this discrepancy.

From a similar study of the OT transition line in the  $T$ - $c$  plane it is found that a good fit is obtained with  $V=0.20 \pm 0.02$  eV. It is also evident from the  $T$ - $c$  plane that the Bragg-Williams approximation (BWA) used by some authors<sup>4,11</sup> is incapable of reproducing the three transition points at 690, 490, and 440  $^{\circ}C$ .

The pair fractional site occupancies  $q$ , obtained in the QCA are shown in Fig. 5 for the  $(440, P)$ ,  $(490, P)$  and

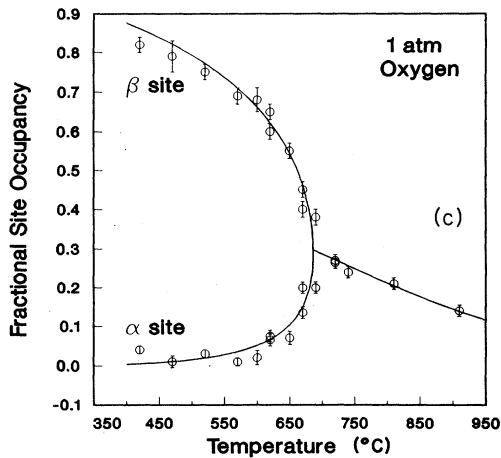
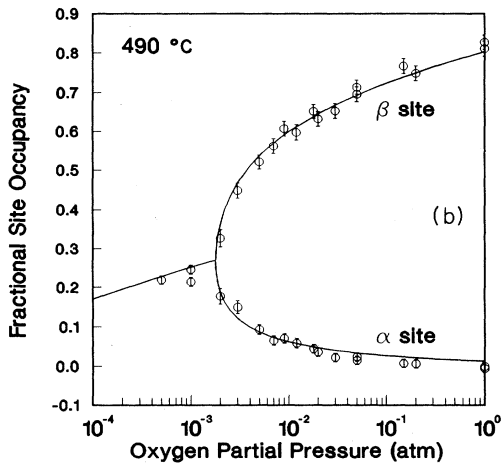
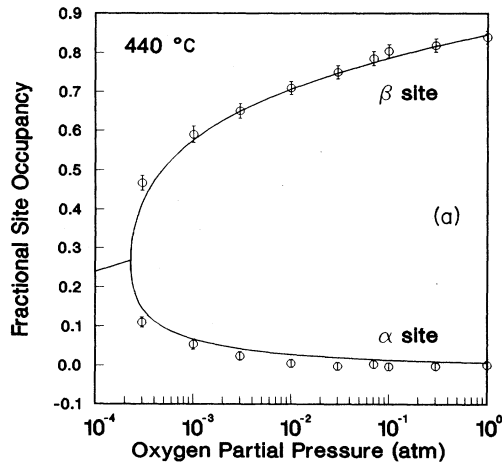


FIG. 3. The observed site occupancies (circles) and the corresponding site occupancies calculated using the QCA (solid lines), (a) as a function of oxygen partial pressure at 440 °C, (b) as a function of oxygen partial pressure at 490 °C, and (c) as a function of temperature at oxygen partial pressure of 1 atm.

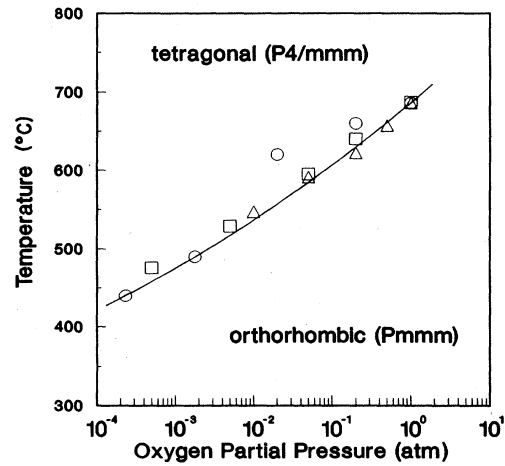


FIG. 4. The orthorhombic-to-tetragonal transition as obtained from neutron diffraction (Refs. 2 and 12) (circles), resistivity measurements (Ref. 3) (squares), and thermogravimetry (Ref. 4) (triangles). The transition line predicted by the QCA is also shown (solid line).

( $T, 1$ ) experiments. At the OT transition,  $q = 4c(c - 0.25)/3$ , whereas, in the completely random ( $T \rightarrow \infty$ ) situation,  $q_r = c^2$  or  $c_\alpha c_\beta$  in the tetragonal or orthorhombic phase, respectively. Values of  $q$  predicted by the QCA are only a few percent of  $q_r$  (except at very high temperature where at 1000 °C,  $q$  is 18% of  $q_r$ ). Hence, in the QCA, oxygen practically avoids an  $\alpha$  site nearest to an occupied  $\beta$  site.

Undoubtedly, the most exciting result of the present work, apart from the excellent agreement of the QCA with experiments (Figs. 3 and 4), is the dependence of the heat of solution  $E$  on the temperature and concentration [Eq. (5) and Fig. 2]. The heat of solution can be expressed as

$$E = \varepsilon + E_d/2, \tag{9}$$

where  $\varepsilon$  is the site energy (or binding energy) and  $E_d$  is the dissociation energy of the oxygen molecule and is

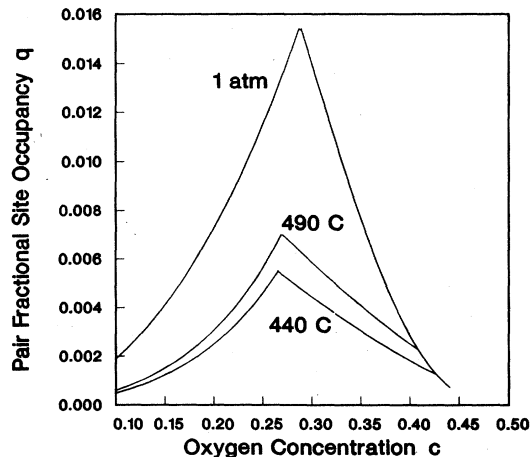


FIG. 5. Fractional site occupancy for NN  $\alpha$ - $\beta$  pairs  $q$  calculated using the QCA for the indicated neutron experiments.

equal to  $5.18 - 3kT/2$  eV.<sup>15</sup> The temperature dependence of  $E_d$  will account only for about 20% of the temperature dependence of  $E$  found in the present work [Eq. (5)]. Hence, it is the site energy  $\varepsilon$  that is responsible for the concentration dependence and for most of the temperature dependence in  $E$ . The linear temperature dependence of  $\varepsilon$  is probably related to the nearly linear thermal expansion of the lattice and is not very interesting. The concentration dependence, on the other hand, has some remarkable features. It shows (Fig. 3) two distinct regions:  $c < 0.25$ , where the compound is an insulator, and  $c > 0.25$  where the compound is a conductor. It should be pointed out that at  $c = 0.25$ , copper is formally at its stable divalent state.

One possible explanation for this dependence is that as  $c$  is increased above 0.25, electrons have to be extracted (from ions or electron bands). As electrons are extracted the energy cost becomes increasingly high. At  $c = 0.5$ , ( $x = 1$ ) an electron per unit cell has been extracted. This could correspond to a density of states at the Fermi level of  $[5.9(0.25)^2]^{-1} \sim 2.7$  eV<sup>-1</sup>, which is similar to the density obtained in detailed electron local-density calculations.<sup>16</sup> On the other hand, it is possible that the concentration dependence of  $\varepsilon$  is of an entirely different nature. The quadratic dependence is very suggestive of oxygen-oxygen interaction. The QCA used in the present analysis includes nearest-neighbor (NN) interaction between  $\alpha$  and  $\beta$  oxygens (Fig. 1) only. The next-nearest-neighbor (NNN) interaction has a range of length  $a$  as compared to  $a/\sqrt{2}$  for the NN interaction. As  $c$  increases above 0.25 ( $x = 0.5$ ) the  $\alpha$  sublattice rapidly becomes practically vacant, while the  $\beta$  sublattice fills up. Hence, the contribution of the NNN  $\beta$ - $\beta$  interaction to the site energy is expected to increase steeply as  $c$  is increased above 0.25. Consider for example the  $\beta$ - $\beta$  oxygen pairs which are  $a$  apart, their number is larger than the number of NN  $\alpha$ - $\beta$  pairs by nearly two orders of magnitude for  $c \sim 0.42$ . There are two different types of NNN  $\beta$ - $\beta$  interactions (Fig. 1), a direct (along  $a$ ) and indirect (mediated by

copper, along  $b$ ). The former is of electrostatic nature whereas the latter is related to the bonding chemistry of copper which prefers the tetraplanar arrangement.

The applicability of the QCA, as demonstrated by the good agreement with experiments (Figs. 3 and 4), has an interesting consequence regarding the concentration at the OT transition. In the QCA the orthorhombic phase exists only for  $0.25 < c < 0.75$ . Under the assumption that oxygen sites other than O(1) ( $\beta$ ) and O(5) ( $\alpha$ ) are fully occupied, this corresponds to  $0.5 < x < 1.5$ . However, recently it was found<sup>12</sup> that O(4) site (in BaO planes) is about 5% vacant at the OT transition. Consequently, reported (equilibrium) orthorhombic structures with  $x$  as low as  $\sim 0.4$  are not inconsistent with this important result [i.e.,  $c(\text{orthorhombic}) > 0.25$ ] of the QCA. The applicability of the QCA also demonstrates the importance of the NN  $\alpha$ - $\beta$  pair occupancy,  $q$  (Fig. 5). The BWA which uses the random pair occupancy (no short-range order) is incapable of reproducing the experimental results. It is only the QCA which includes short-range order, leading to extremely low pair occupancies which agrees with experiments.

In summary, it is found that the two oxygen site occupancies in the CuO planes, calculated using the QCA, are in good agreement with experiments. These calculations yield (i) An extremely low NN  $\alpha$ - $\beta$  pair site occupancy; (ii) a constant NN oxygen repulsion energy  $V = 0.2 \pm 0.02$  eV; and (iii) a site (binding) energy linear in temperature, quadratic in the oxygen concentration in the orthorhombic phase, and independent of oxygen concentration in the tetragonal phase. Possible mechanisms for this remarkable behavior of the site energy are discussed.

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<sup>1</sup>J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, *Phys. Rev. B* **36**, 5731 (1987).

<sup>2</sup>J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, *Phys. Rev. B* **36**, 3608 (1987).

<sup>3</sup>P. P. Freitas, and T. S. Plaskett, *Phys. Rev. B* **36**, 5723 (1987).

<sup>4</sup>Y. Kubo, Y. Nakabayashi, J. Tabuchi, T. Yoshitake, A. Ochi, K. Utsumi, H. Igarashi, and M. Yonezawa, *Jpn. J. Appl. Phys.* **26**, L1888 (1987).

<sup>5</sup>K. Kishio, J. Shimoyana, T. Hasegawa, K. Kitazawa, and K. Fueki, *Jpn. J. Appl. Phys.* **26**, L1228 (1987).

<sup>6</sup>E. D. Specht, C. J. Sparks, A. G. Dhere, J. Brynstad, O. B. Cavin, D. M. Kroeger, H. A. Oye, and F. J. Seiler, *Phys. Rev. B* **37**, 7426 (1988).

<sup>7</sup>W. R. McKinnon, M. L. Post, L. S. Selwyn, G. Pleizier, J. M. Tarascon, P. Barboux, L. H. Greene, and W. Hull, *Phys. Rev. B* **38**, 6543 (1988).

<sup>8</sup>H. Bakker, D. O. Welch, and O. W. Lazareth, Jr., *Solid State*

*Commun.* **64**, 237 (1987); H. Bakker, J. P. A. Westerveld, D. M. R. Lo Cascio, and D. O. Welch (unpublished).

<sup>9</sup>E. Salomons, N. Koeman, R. Brouwer, D. G. de Groot, and R. Greissen, *Solid State Commun* **64**, 1141 (1987).

<sup>10</sup>L. T. Wille, A. Berera, and D. de Fontaine, *Phys. Rev. Lett.* **60**, 1065 (1988).

<sup>11</sup>K. Nakamura and K. Ogawa (unpublished).

<sup>12</sup>J. D. Jorgensen, H. Shaked, D. G. Hinks, B. Dabrowski, B. W. Veal, A. P. Paulikas, L. J. Nowicki, G. W. Crabtree, W. K. Kwok, and L. H. Nunez, *Physica C* **153-155**, 578 (1988).

<sup>13</sup>M. A. Beno, L. Soderholm, D. W. Capone II, D. G. Hinks, J. D. Jorgensen, J. D. Grace, I. K. Schuller, C. U. Segre, and K. Zhang, *Appl. Phys. Lett.* **51**, 57 (1987).

<sup>14</sup>T. Muto, and Y. Takagi, *Solid State Physics*, edited by R. Seitz and D. Turnbull (Academic, New York, 1955), Vol. 1, p. 193.

<sup>15</sup>J. A. Kerr, and A. F. Trotman-Dickenson, *Handbook of Chemistry and Physics*, 62nd ed. (CRC, Boca Raton, FL, 1981), p. F-180.

<sup>16</sup>S. Massida, J. Yu, A. J. Freeman, and D. D. Koelling, *Phys. Lett. A* **122**, 198 (1987).