

The Oxidation State of Pr in PrBa₂Cu₃O₇¹

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PrBa₂Cu₃O₇ is isostructural with YBa₂Cu₃O₇, yet it is not a superconductor. We have performed a variety of experiments to determine the valence of Pr in this material. We report on the results of synthetic trend studies, powder neutron diffraction, X-ray absorption spectra, and magnetic susceptibility experiments and offer our analysis of the contribution that each makes to the overall understanding of the electronic behavior of Pr in this compound. Since Pr⁴⁺ is relatively stable, and since Pr is known to form mixed-valent alloys, the suggestion had been made that Pr⁴⁺ might be inhibiting superconductivity through an *in situ* oxidation reduction reaction with the Cu-O bands. We conclude that Pr is essentially trivalent in PrBa₂Cu₃O₇. © 1989 Academic Press, Inc.

Introduction

Shortly after the initial reports that YBa₂Cu₃O₇, known as Y123O₇, is a superconductor with a transition temperature (T_c) of 92 K (1), it became clear that Y could be replaced by most of the rare-earth ions without destroying the superconductivity (2, 3). This was an unexpected finding, since most of the rare-earth ions have unpaired *f*-electrons and hence they carry substantial magnetic moments. In the more conventional alloy superconductors, it has been well established that the introduction of even low, dopant levels of a magnetic ion quickly inhibits the superconductivity, presumably by interfering with the formation of Cooper pairs. Some magnetic rare-earth ternary superconductors have been re-

ported, where presumably there is little interaction between the unpaired *f*-electrons and the conduction electrons (4).

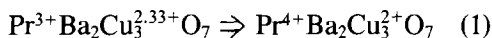
While most of the rare earths can fully substitute for Y without significantly altering T_c , there are three exceptions: the replacement of Y with Ce, Pr, or Tb does not result in a superconducting material (2, 3). In fact, neither Ce nor Tb forms a single-phase compound with the 1 : 2 : 3 stoichiometry under the standard synthetic conditions. Instead the reactants combine to form the perovskite phase BaMO₃ ($M = Ce$ or Tb), plus the impurity phases necessary to account for the starting stoichiometry. Even attempts to substitute partially Ce or Tb for Y, to form a solid solution of the type (Y_{1-x}Ce_x,Tb_x)Ba₂Cu₃O₇, have not resulted in demonstrably single-phase samples.

In contrast with the behavior of Ce and Tb is the behavior of Pr in this system. Pr can be incorporated into the Y123O₇ phase, totally replacing Y, while retaining the

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orthorhombic structure characteristic of the $R123O_7$ (R = rare earth) superconductors. However, $Pr123O_7$ is not a superconductor (5, 6). This absence of superconductivity in the Pr compound, which has the orthorhombic $Pmmm$ $Y123O_7$ structure, needs to be explained.

Since Ce, Pr, and Tb are the three rare earths that are most readily oxidized to the tetravalent state (7), it has been suggested that the lack of superconductivity in $Pr123O_7$ is somehow related to this fact. For example, the Pr could serve as an *in situ* reducing agent for the copper:



Since the removal of oxygen from $Y123O_7$ also has the net effect of reducing the copper, and since the oxygen content in $Y123O_x$ correlates with T_c (8), a mechanism for suppressing T_c involving the formal reduction of copper appears quite plausible. This mechanism, involving Pr^{4+} , seemed even more probable after initial work on the resistivity and critical temperature behavior in the solid-solution series $Y_{1-x}Pr_xBa_2Cu_3O_7$ (6) was found to be consistent with the reduction of the copper valence. Subsequent to this initial work, however, a variety of results has brought into question the validity of this simple interpretation of the resistivity behavior of these compounds.

Up to now, the question of the valence of Pr in $Pr123O_7$ has not been resolved, and its mechanism for suppressing the superconductivity seen in other rare-earth analogs of $Y123O_7$ is not understood. We believe that the details of the mechanism for suppression of T_c in the Pr compound will provide important insight into the overall mechanism responsible for high T_c superconductivity in the other members of the $R123O_7$ series. Fundamental to understanding the mechanism is a knowledge of the electron distribution within the solid, and therefore the oxidation state of Pr in $Pr123O_7$. Here we report the results of a variety of experi-

ments toward this end and comment on the overall understanding of the electronic behavior of Pr in $Pr123O_7$.

Experimental

The samples were prepared by standard ceramic techniques. Stoichiometric amounts of Ln_2O_3 (Ln = lanthanide or Y) or Pr_6O_{11} , $BaCO_3$, and CuO were intimately mixed, placed in gold boats, and fired at 990°C. These samples were then reground and refired under flowing O_2 , followed by slow cooling. The sample purity was initially checked by X-ray diffraction, utilizing a Scintag theta-theta diffractometer equipped with a solid-state detector. The samples were often found to contain $BaCuO_2$ and CuO as impurity phases. This difficulty was overcome by starting with a slight excess of Pr in the preparations, such that the stoichiometry of our $Pr123O_7$ was in fact $Pr_{1.06}Ba_{1.94}Cu_3O_7$. This was the nearest that we could come to the stoichiometric compound with our synthetic procedure. Samples were further characterized by magnetic susceptibility measurements on a George Associates Magnetometer and by neutron diffraction, utilizing the general purpose powder diffractometer (GPPD) at the intense pulsed neutron source at Argonne National Laboratory. These powder patterns were fit with a standard Rietveld fitting program (9).

Results and Discussion

Structural Studies

Trends in structural features, such as systematic changes in lattice constants or bond lengths across an isostructural series of compounds, have often been used as indicators of the sizes or charges for ions in a solid. In fact, the reference tables reporting ionic radii are based on just such trends. While these studies are most informative

when done on binary systems with simple structures, limited information can sometimes be obtained from more complex compounds such as the oxides under consideration here.

Pr123O₇ is a member of the isostructural series R123O₇ (R = Y, La, Pr–Er), which crystallize in a rather complex, orthorhombic structure, typified by Y123O₇ (10). Within this series, the *a* and *b* cell lengths have been shown to increase slightly with increasing rare-earth radius. Assuming the radius of Pr³⁺ (11), the cell lengths determined by powder neutron diffraction for Pr123O₇ (*a* = 3.8920(1), *b* = 3.9123(1)) fit well with the trend established by the R³⁺123O₇ compounds (3).

It has also been previously noted that as the rare-earth radius increases, the degree of orthorhombic distortion, defined as

$$d_{or} = 200(b - a)/(b + a),$$

decreases as the rare-earth size increases. The value of $d_{or} = 0.52$ for the Pr compound, may be slightly smaller than expected on the basis of a similar analysis of the La ($d_{or} = 0.56$) (12), Nd ($d_{or} = 1.2$), Y ($d_{or} = 1.6$) (10), or Ho ($d_{or} = 1.6$) (13) data, but, as with the cell lengths, the Pr sample does follow the general trend.

While we can see trends in the *a* and *b* lattice constants with change in the size of the rare earth, this is not the case for the *c* axis length. Although the Cu₂–Cu₂ distance increases with size of *R*, the Cu₁–Cu₂ distance decreases. The *c* axis length is a sum

$$L_{c-axis} = 2(\text{Cu1-Cu2}) + (\text{Cu2-Cu2}),$$

so that no overall trend can be seen.

In general, because of the complexity of the 1 : 2 : 3 structure, it is more informative to look directly at trends in the *R*–O bond distances, rather than at the lattice constants. A plot of the average *R*–O bond distance vs the R³⁺ ionic radius is shown in Fig. 1. The *R*–O bond distances used in this

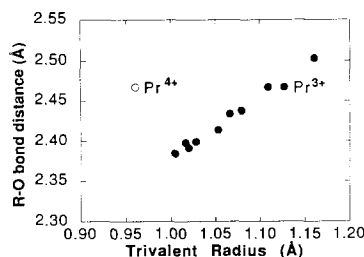


FIG. 1. The *R*–O average bond distance vs the eight-coordinate, trivalent, rare-earth ionic radius (11). Bond distances are reported from neutron diffraction results (10, 12, 13, this work) where available; otherwise they are taken from single-crystal X-ray results (14). Also plotted, for comparison, is the *R*–O bond distance vs the tetravalent Pr ionic radius.

figure are obtained simply by averaging the two different bond distances obtained from refined neutron powder data. Where neutron data are unavailable, we have substituted single-crystal X-ray data available in the literature (10, 12–14). As can be seen, there is a very good correlation between the average bond distance and the trivalent rare-earth radius. The data for Pr–O fit just off this line if a trivalent radius is chosen. For comparison, the Pr–O distance is also plotted against the Pr⁴⁺ ionic radius, which is well off the line representing the trend of the other ions. If the O²⁻ radius (11) is subtracted from the *R*–O experimentally determined distance, the radius of R³⁺ is obtained and agrees well with the literature values for all the rare earths, including Pr³⁺.

Pr123O₇ follows the trends in cell constants and *R*–O bond distances which are established by the isostructural R³⁺123O₇ compounds. From this behavior, we conclude that the size of Pr is consistent with Pr³⁺. These structural data form a strong argument in favor of an essentially trivalent Pr in Pr123O₇.

The Relative Stabilities of the Phases R_{1+x}Ba_{2-x}Cu₃O₇

Within the series RBa₂Cu₃O_x, the stoichiometry 1 : 2 : 3 becomes increasing more

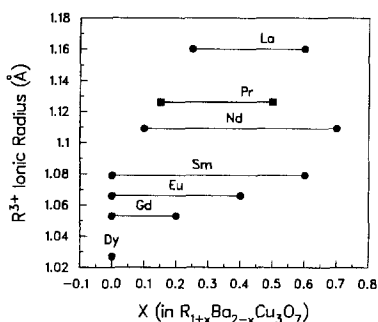


FIG. 2. The stability range for the formation of the solid solution $R_{1+x}Ba_{2-x}Cu_3O_7$ under similar synthetic conditions, optimized for $Y123O_7$. The Pr results are consistent with the trend established by the trivalent rare earths.

difficult to stabilize as the rare earth becomes larger. La, the largest of the lanthanides, is the most difficult to substitute for Y, often producing multiphase samples with low T_c 's (15). Instead of forming the 123 phase, La partially replaces Ba, to form the solid solution $La_{1+y}Ba_{2-y}Cu_3O_x$, $0 \leq y \leq 0.6$ (16). Since these materials are synthesized in the solid state, $BaCuO_2$ and CuO are found as impurity phases in these cases. The solid solution stability range is very dependent on the details of synthetic conditions such as temperatures of firing and annealing as well as cooling rates. As the rare earth becomes smaller, the maximum value of y decreases, until at $Dy123O_x$ there is no evidence for the presence of any Dy on the Ba site; that is there is no solid solution of the form $Dy_{1+y}Ba_{2-y}Cu_3O_x$ (17, 18). The tendency of the lighter rare earths to substitute for Ba is probably the direct result of the size of the rare-earth ion, which can disorder on the Ba site only with the larger trivalent cations.

The systematics of this phase formation and the limits of the phase lines have been previously demonstrated for Y, La, and Nd–Dy (17). This was accomplished by fixing the synthetic conditions as optimized for Y123. Systematic changes in lattice con-

stants, together with the appearance of impurity lines in the X-ray diffraction patterns, were used to judge the sample purity. (We have found that changes in lattice constants are often a more sensitive indication of compositional variation than the absence of extraneous diffraction peaks.) As in previous cases, a solid solution, plus the impurity phases $BaCuO_2$ and CuO , was formed. The stability limits of the trivalent rare earths can be seen to form a consistent trend as shown in Fig. 2. Following the same procedure as that for Pr, the pure $Pr123O_x$ compound could not be formed under these strict synthetic conditions. The single-phase region is $Pr_{1+y}Ba_{2-y}Cu_3O_x$, $0.1 \leq y \leq 0.5$. These results, also shown in Fig. 2, are essentially consistent with the results of the other trivalent rare earths, although the upper limit of Pr substitution is less than expected from the La and Nd results. Since the stability of these solid solutions is thought to be dependent on the size of the rare-earth ion, we interpret this similarity in stability behavior between Pr and its neighboring trivalent ions as evidence that Pr is also trivalent in $Pr123O_7$.

Magnetic Susceptibility

Much of the literature published to date has relied on the interpretation of magnetic susceptibility data as a means of determining the oxidation state of Pr in $Pr123O_7$. Because of the low site symmetry at Pr (mmm) (10), a thorough interpretation of such data is complex, time consuming, and dependent on additional information, such as that obtained from optical or inelastic neutron data. Instead of this complex approach, a much simpler method of data interpretation, involving several assumptions, has often been used. Below, we attempt to outline this method as applied to the problem at hand.

The variation of the magnetic susceptibility with temperature can be related to the

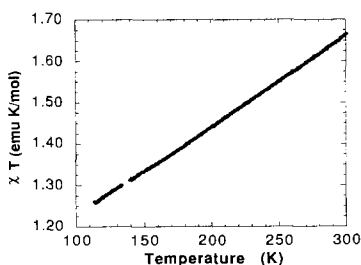


FIG. 3. The magnetic susceptibility of Pr123O₇ as a function of temperature. An effective moment of 2.84 μ_B is extracted from these data. This value is intermediate between that expected for the Pr³⁺ (3.58 μ_B) and the Pr⁴⁺ (2.54 μ_B) free ions.

oxidation state of an ion by fitting the data to

$$\chi = C/(T + \theta) + \chi_0, \quad (2)$$

where χ_0 is a temperature-independent term, and θ is a parameter to account for short-range ordering effects. C , the Curie constant, is related to the effective moment μ_{eff} , by

$$C = N(\mu_{\text{eff}})^2/(3k_B). \quad (3)$$

Here, N is Avogadro's number and k_B is Boltzmann's constant. In the simplest case, the effective moment of an ion can be related to its oxidation state by

$$\mu_{\text{eff}} = g_J(J(J + 1))^{1/2} \mu_B, \quad (4)$$

where g_J is the Lande g -factor, and $J (= L \pm S)$ is the total angular momentum for the Russell-Saunders ground state, which differs for each oxidation state of an ion. Inherent in this interpretation of the susceptibility are the assumptions that (i) the spins are not interacting and (ii) there are no low-lying excited states which are being significantly populated over the temperature range under investigation.

Susceptibility data obtained from Pr123O₇ are shown in Fig. 3. The value of the effective moment, determined using this approach, is compared with representative literature values in Table I. While

there are some variations in the listed experimental effective moments, they are all intermediate between that expected for a Pr³⁺ (f^2 , $\mu_{\text{FI}} = 3.58 \mu_B$) and a Pr⁴⁺ (f^1 , $\mu_{\text{FI}} = 2.54 \mu_B$) free ion. Since this simple procedure does not produce the free ion value expected for either of the two possible oxidation states, these results are ambiguous.

In order to derive further information from these data while continuing to use the concepts of this simple model, some authors have assumed that Pr is not simply trivalent or tetravalent, but should instead be treated as a mixed-valent system, that is a mixture of Pr³⁺ and Pr⁴⁺. Presumably this assumption is based on the behavior of Pr in selected alloy systems. In this case it is a doubtful approach, since these Pr ions are all crystallographically equivalent in Pr123O₇. Assuming two types of noninteracting magnetic spins, the total susceptibility is then treated as a weighted sum of the individual susceptibilities, permitting the decomposition of the experimental susceptibility into

$$\chi_{\text{exp}} = a\chi_{\text{Pr}^{3+}} + (1 - a)\chi_{\text{Pr}^{4+}}, \quad (5)$$

where a represents the mole fraction of Pr³⁺. There is now one equation and three unknowns, necessitating some additional assumptions about the effective moments of Pr³⁺ and Pr⁴⁺. Their free ion values have

TABLE I
THE REPORTED EFFECTIVE MOMENTS OF Pr IN Pr123O₇ AS DETERMINED BY FITTING MAGNETIC SUSCEPTIBILITY DATA WITH THE CURIE WEISS LAW

μ_{eff} (μ_B)	TIP ($\times 10^4$)	Pr valence	Reference
3.38	0.	3.4	(19)
2.94	0.968	3.9	(20)
3.06–2.79	—	3.5–3.8	(21)
2.67	—	3.9	(22)
3.0	0.028	3.5	(23)
2.84	0.28	3.7	This work

Note. The average valence is determined from a simple, mixed-valent model, as discussed in the text.

always been taken for the analyses of the Pr123O_7 data. Utilizing these assumptions, it is possible to obtain an average oxidation state for Pr. The value of the average Pr oxidation states listed in Table I are obtained in this manner.

Unfortunately, there are no independent data supporting the presence of mixed valent Pr in this material. Even if the mixed valent approach were correct, the assumption that Pr behaves like a free ion in this environment is not supported by the literature. For example, using the same procedure as that outlined above, the oxidation state of Pr in PrScO_3 is found to be $3.5+$ (24). PrScO_3 is a perovskite, and the Pr finds itself on a site with symmetry similar to that found in Pr123O_7 . The compound is light green and nonmetallic, and the oxygen content was determined to be very close to stoichiometry. The presence of even small amounts of Pr^{4+} would be expected to render the sample black. Therefore the conclusion that the susceptibility of Pr is lower than that expected for Pr^{3+} simply because of the presence of Pr^{4+} is very unlikely for PrScO_3 . Furthermore a substantially reduced moment has been found for tetravalent Pr in BaPrO_3 , where calculations show that the effective moment of $0.71 \mu_B$ can be accounted for by the effect of the crystal field (25). On the other hand, tetravalent Pr in PrO_2 has a nearly free ion moment of $2.47 \mu_B$.

An alternate explanation for the intermediate value of the experimentally determined effective moment could be a strong interatomic hybridization of the Pr f -electrons with the Cu–O conduction electrons. This covalent bonding would provide a mechanism for reducing the orbital (L) contribution to the total angular momentum (J). This mechanism for moment reduction is not consistent with the simple interpretation (Eq. (4)) outlined above, and would instead require a model involving some type of orbital reduction factor to treat the susceptibility.

To summarize the results of the magnetic susceptibility experiments, the observed experimental effective moments that are intermediate between those expected for Pr^{3+} and Pr^{4+} could be interpreted in terms of either crystal field effects or intermediate valence or mixed valence. These are three distinct mechanisms for reducing the observed moment which cannot be distinguished by susceptibility results alone. In the absence of other, independent data, the susceptibility data do not contribute significantly to our understanding of the distribution of electron density in Pr123O_7 .

XANES

X-ray absorption measurements provide a tool for the determination of metal oxidation states in solids (26). The technique utilizes subtle changes in K , L , M , . . . absorption edges of an ion in a solid with respect to standard compounds with known oxidation states as an indication of the oxidation state of an ion in the solid, in a manner similar to the use of isomer shifts and hyperfine effects in Mössbauer spectroscopy. Several advantages to this technique for the problem at hand include ambient temperature and pressure data collection, which substantially reduces sample degradation associated with the high oxygen mobility in these samples (8, 27). Furthermore, this is a single-ion probe with a very fast time scale ($\approx 10^{-16}$ sec) so that the presence of more than one electronic type in the sample, as expected for a mixed-valent system, should be observable as a combination of two spectra. On the other hand, an intermediate valent system, arising from a strongly covalent environment, should also be discernible.

Figure 4 shows data obtained for Pr123O_7 , together with a trivalent (Pr_2O_3) and a tetravalent (PrO_2) oxide standard. It can be clearly seen that as the oxidation state of Pr increases, the L_{III} -absorption edge shifts to higher energy. Furthermore, the edge appears more complex for the

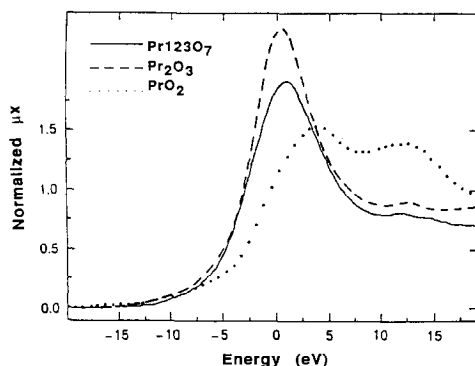


FIG. 4. L_{III} -edge X-ray absorption data (XANES) comparing a Pr^{3+} (Pr_2O_3) and a Pr^{4+} (PrO_2) standard with $\text{Pr}_{123}\text{O}_7$ (28). The similarity in the edge features of $\text{Pr}_{123}\text{O}_7$ and the trivalent standard is strong evidence that Pr is essentially trivalent in $\text{Pr}_{123}\text{O}_7$.

tetravalent case. By comparison of the edge obtained for $\text{Pr}_{123}\text{O}_x$ with the two standards, there are two things which are clear. There is no evidence either of an edge shift toward the tetravalent standard, as would be expected for an intermediate-valent system, or of two distinct absorptions, as expected for mixed valent Pr. These data show Pr to be essentially trivalent in $\text{Pr}_{123}\text{O}_7$ (28). Other X-ray absorption studies on $\text{Pr}_{123}\text{O}_7$ and $(\text{Y}_{1-x}\text{Pr}_x)\text{123O}_7$ have produced similar conclusions (29).

Conclusions

We report the results of several experiments carried out to ascertain the oxidation state of Pr in $\text{Pr}_{123}\text{O}_7$. We find that Pr is trivalent, on the basis of structure and chemical stability studies. Pr L -edge X-ray absorption edges confirm this finding. Magnetic susceptibility data are similar to those previously published, but are judged to produce results too ambiguous to analyze in the absence of a more detailed knowledge of the formalism appropriate for data treatment.

Inherent in our discussion of the oxidation state of Pr is the simple assumption of integral valence, i.e., that Pr is either triva-

lent or tetravalent. We do not rule out the possibility of small amounts of mixed-valent or intermediate-valent behavior, but we do rule out the possibility of an average oxidation state substantially different from trivalent. In fact, since $\text{Pr}_{123}\text{O}_7$ is orthorhombic but not superconducting, and since Pr is essentially trivalent, we expect that some mechanism involving a slight coupling of Pr f -electrons to the conduction electrons is responsible for the lack of superconductivity. Experiments designed to differentiate between various coupling models are currently under way.

Acknowledgments

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References

1. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG, AND C. W. CHU, *Phys. Rev. Lett.* **58**, 908 (1987).
2. (a) P. H. HOR, R. L. MENG, Y. Q. WANG, L. GAO, Z. J. HUANG, J. BECHTOLD, K. FORSTER, AND C. W. CHU, *Phys. Rev. Lett.* **58**, 1891 (1987); (b) S. E. BROWN, J. D. THOMPSON, J. O. WILLIS, R. M. AIKEN, E. ZIRGNIEBL, J. L. SMITH, Z. FISK, AND R. B. SCHWARZ, *Phys. Rev. B* **36**, 2298 (1987); (c) J. M. TARASCON, W. R. MCKINNON, L. H. GREENE, G. W. HULL, AND E. M. VOGEL, *Phys. Rev. B* **36**, 226 (1987).
3. L. F. SCHNEEMEYER, J. V. WASZCZAK, S. M. ZAHURAK, R. B. VAN DOVER, AND T. SIEGRIST, *Mater. Res. Bull.* **22**, 1467 (1987).
4. See, for example, "Ternary Superconductors" (G. K. Shenoy, B. D. Dunlap, and F. Y. Fradin, Eds.), North Holland, New York (1981).
5. D. W. MURPHY, S. SUNSHINE, R. B. VAN DOVER, R. J. CAVA, B. BATLOGG, S. M. ZAHURAK, AND L. F. SCHNEEMEYER, *Phys. Rev. Lett.* **58**, 1888 (1987).
6. L. SODERHOLM, K. ZHANG, D. G. HINKS, M. A. BENO, J. D. JORGENSEN, C. U. SEGRE, AND IVAN K. SCHULLER, *Nature (London)* **328**, 604 (1987).
7. LESTER R. MORSS, in "Standard Potentials in Aqueous Solution" (Allen J. Bard, Roger Parsons,

- and Joseph Jorden, Eds.), Chap. 20, Dekker, New York (1985).
8. (a) D. C. JOHNSTON, A. J. JACOBSON, J. M. NEWSAM, J. T. LEWANDOWSKI, D. P. GOSHORN, D. XIE, AND W. B. YELON, in "Chemistry of High Temperature Superconductors" (David Nelson, M. S. Whittingham, and Thomas F. George, Eds.), ACS Symposium Series 351, p. 136, Amer. Chem. Soc., Washington, DC; (b) J. JORGENSEN, M. A. BENO, D. G. HINKS, L. SODERHOLM, K. J. VOLIN, R. L. HITTERMAN, J. D. GRACE, IVAN K. SCHULLER, C. U. SEGRE, K. ZHANG, AND M. S. KLEEFISCH, *Phys. Rev. B* **36**(7), 3608 (1987).
 9. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969).
 10. M. A. BENO, L. SODERHOLM, D. W. CAPONE II, D. G. HINKS, J. D. JORGENSEN, IVAN K. SCHULLER, C. U. SEGRE, K. ZHANG, AND J. D. GRACE, *Appl. Phys. Lett.* **51**, 57 (1987).
 11. R. D. SHANNON, *Acta Crystallogr. A* **32**, 751 (1976).
 12. E. M. MCCARRON, C. C. TORARDI, J. P. ATTFIELD, K. J. MORRISSEY, A. W. SLEIGHT, D. E. COX, R. K. BORDIA, W. E. FARNETH, R. B. FLIPPEN, M. A. SUBRAMANIAN, E. LOPDRUP, AND S. J. POON, *Mater. Res. Soc. Symp. Proc.* **99**, 101 (1988).
 13. B. D. DUNLAP, M. SLASKI, D. G. HINKS, L. SODERHOLM, M. BENO, K. ZHANG, C. SEGRE, G. W. CRABTREE, W. K. KWOK, S. K. MALIK, IVAN K. SCHULLER, J. D. JORGENSEN, AND Z. SUNGAILA, *J. Magn. Mater.* **68**, L139 (1987).
 14. Y. LE PAGE, T. SIEGRIST, S. A. SUNSHINE, L. F. SCHNEEMEYER, D. W. MURPHY, S. M. ZAHURAK, J. V. WASZCZAK, W. R. MCKINNON, J. M. TARASCON, G. W. HULL, AND L. H. GREENE, *Phys. Rev. B* **36**, 3617 (1987).
 15. S. KATANO, S. FUNAHASHI, T. HATANO, A. MATSUSHITA, K. NAKAMURA, T. MATSUMOTO, AND K. OGAWA, *Japan. J. Appl. Phys.* **26**, L1046 (1987).
 16. (a) D. B. MITZI, A. F. MARSHALL, J. Z. SUN, D. J. WEBB, M. R. BEASLEY, T. H. GEBALLE, AND A. KAPITULNIK, unpublished; (b) EIJI TAKAYAMA-MUROMACHI, YOSHISHIGE UCHIDA, ATSUSHI FUJIMORI, AND KATSUO KATO, *Japan. J. of Appl. Phys.* **26**, L1546 (1987); (c) J. E. GREEDAN, A. H. O'REILLY, C. V. STAGER, F. RAZAVI, AND W. ABRIEL, *Mater. Res. Soc. Symp. Proc.* **99**, 749 (1988); (d) L. EL-RAKHO, C. MICHEL, J. PROVOST, AND B. RAVEAU, *J. Solid State Chem.* **37**, 151 (1981).
 17. (a) KAIJUN ZHANG, Doctoral thesis, Illinois Institute of Technology (1988); (b) K. ZHANG, B. DABROWSKI, C. U. SEGRE, D. G. HINKS, IVAN K. SCHULLER, J. D. JORGENSEN, AND M. SLASKI, *J. Phys. C* **20**, L935 (1987).
 18. (a) D. G. HINKS, L. SODERHOLM, D. W. CAPONE II, J. D. JORGENSEN, IVAN K. SCHULLER, C. U. SEGRE, K. ZHANG, AND J. D. GRACE, *Appl. Phys. Lett.* **50**, 1688 (1987); (b) L. SODERHOLM, D. W. CAPONE II, D. G. HINKS, J. D. JORGENSEN, IVAN K. SCHULLER, J. GRACE, K. ZHANG, AND C. U. SEGRE, *Inorg. Chim. Acta* **140**, 167 (1987).
 19. E. MORAN, U. AMADOR, M. BARAHONA, M. A. ALARIO-FRANCE, A. VEGAS, AND J. RODRIGUEZ-CARVAJAL, *Solid State Commun.* **67**, 369 (1988).
 20. Y. DALICHAOUCH, M. S. TORIKACHVILI, E. A. EARLY, B. W. LEE, C. L. SEAMAN, K. N. YANG, H. ZHOU, AND M. B. MAPLE, *Solid State Commun.* **65**, 1001 (1988).
 21. D. B. MITZI, P. T. FEFFER, J. M. NEWSAM, D. J. WEBB, P. KLAVINS, A. J. JACOBSON, AND A. KAPITULNIK, *Phys. Rev. B* **38**, 6667 (1988).
 22. BIN OKAI, MICHIKAZU KOSUGE, HIROSHI NOZAKI, KOH TAKAHASHI, AND MASATSUNE OHTA, *Japan. J. Appl. Phys.* **27**(1), L41 (1988).
 23. AZUSA MATSUDA, KYOICHI KINOSHITA, TAKAO ISHII, HIROYUKI SHIBATA, TAKAO WATANABE, AND TOMOSKI YAMADA, *Phys. Rev. B* **38**(4), 2910 (1988).
 24. DAVID A. MACLEAN, KAN SETO, AND J. E. GREEDAN, *J. Solid State Chem.* **40**, 241 (1981).
 25. M. BICKEL, G. L. GOODMAN, L. SODERHOLM, AND B. KANELAKOPOULOS, *J. Solid State Chem.* **76**, 178 (1988); DAVID A. MACLEAN, KAN SETO, AND J. E. GREEDAN, *J. Solid State Chem.* **40**, 241 (1981).
 26. (a) ALAIN MOSSET AND JEAN GALY, in "Topics in Current Chemistry" (E. Mandelkow, Ed.), Vol. 145, p. 1; (b) L. SODERHOLM AND G. L. GOODMAN, *J. Opt. Soc. Amer. B*, **6**, 483 (1989).
 27. (a) W. HERZOG, M. SCHWARZ, H. SIXL, AND R. HOPPE, *Z. Phys. B* **71**, 19 (1988); (b) R. S. LIST, A. J. ARKO, Z. FISK, S.-W. CHEONG, S. CONRADSON, J. D. THOMPSON, B. PIERCE, D. E. PETERSON, R. BARTLETT, N. D. SHINN, J. E. SCHIRBER, B. W. VEAL, A. P. PAULIKAS, AND J. C. CAMPUZANO, preprint; (c) P. STEINER, V. KINSINGER, I. SANDER, B. SIEGWART, S. HUFNER, C. POLITIS, R. HOPPE, AND H. P. MULLER, *Z. Phys. B* **67**, 497 (1987).
 28. E. E. ALP, L. SODERHOLM, G. K. SHENOY, D. G. HINKS, B. W. VEAL, AND P. A. MONTANO, *Physica B* **150**, 74 (1988).
 29. (a) U. NEUKIRCH, C. T. SIMMONS, P. SLADACEK, C. LAUBSCHAT, O. STREBEL, G. KAINDL, AND D. D. SARMA, *Europhys. Lett.* **5**(6), 567 (1988); (b) F. W. LYTLE, R. B. GREGOR, E. M. LARSON, AND J. WONG, preprint.