PHYSICAL REVIEW B VOLUME 51, NUMBER 17 1 MAY 1995-I

Role of Ba-site Pr in quenching superconductivity of $Y_{1-y}Pr_yBa_2Cu_3O_x$ and related materials

Howard A. Blackstead
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

John D. Dow
Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504

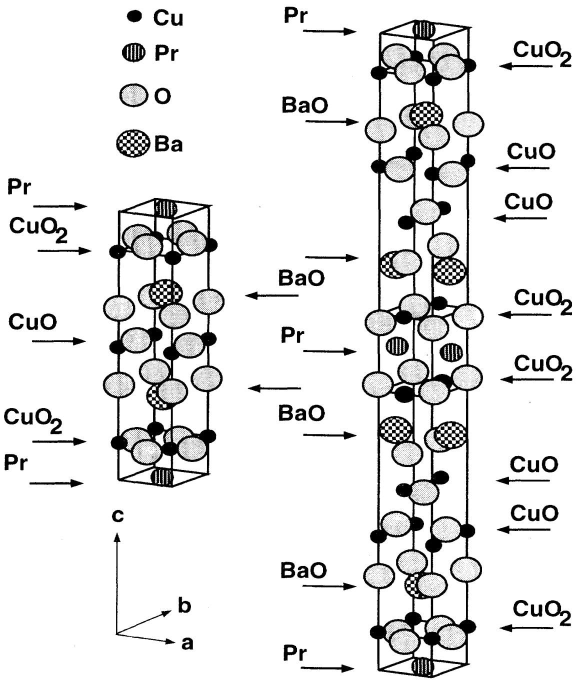
(Received 19 May 1994)

The depression of the superconducting transition temperature with increasing Pr content y in $Y_{1-y}Pr_yBa_2Cu_3O_x$ (for $x \approx 7$) is ascribed primarily to the breaking of Cooper pairs *in chain layers* by Ba-site Pr^{+3}.

I. INTRODUCTION

Materials of the (rare-earth)$Ba_2Cu_3O_x$ class with oxygen content $x \approx 7$ superconduct at critical temperatures of about $T_c \approx 90$ K not only for Y on the rare-earth site but also for the following rare earths on that site: La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu.[1] Only Ce, Pr, and Tb of the rare earths do not form *single-phase superconducting* material with the same crystal structure.[2–5] However, partial Tb substitution in thin-film and bulk $Y_{1-y}Tb_yBa_2Cu_3O_x$ (for $y<0.5$) (Refs. 6 and 7) does produce a superconductor whose superconductivity is not degraded by the Tb,[3] and so we assume that $TbBa_2Cu_3O_x$, if it were crystallographically stable, would superconduct. $Y_{1-y}Pr_yBa_2Cu_3O_x$ with $x \approx 7$ forms single-phase material for all Pr contents y. This material superconducts with monotonically decreasing transition temperature up to $y \approx 0.5$, beyond which the superconductivity is quenched, and then the material becomes an insulator for $y \rightarrow 1$.[8–12] Ce, like Tb, partially substitutes for Y in $Y_{1-y}Ce_yBa_2Cu_3O_x$ thin films, but, unlike Tb, degrades the superconductivity much as Pr does in $Y_{1-y}Pr_yBa_2Cu_3O_x$.[6] Ce doping of $NdBa_2Cu_3O_x$ is also deleterious to superconductivity.[13] Hence we classify hypothetical $CeBa_2Cu_3O_x$ as an insulator similar to $PrBa_2Cu_3O_x$. Thus, of the rare earths, only Ce and Pr replacing Y in $YBa_2Cu_3O_x$ fail to produce ≈ 90 K superconductivity under standard conditions of synthesis.[14] Therefore the natural question to be answered by any successful theory of high-temperature superconductivity[15–18] is why does $PrBa_2Cu_3O_x$ *not* superconduct.

To date, the primary reasons given to explain the anomalous behavior of $PrBa_2Cu_3O_x$ (Refs. 2 and 6) can be classified as either (i) charge fluctuations and hole filling: Pr is either always or sometimes in the Pr^{+4} state,[4] in contrast with most of the rare earths that lead to superconductivity, which are in the (rare-earth)$^{+3}$ charge state (the extra Pr electron supposedly fills and annihilates a hole in an adjacent cuprate plane that would otherwise be involved in superconductivity); or (ii) spin fluctuations and pair breaking: magnetic interactions involving charge carriers destroy the superconductivity when Pr is present. The most common spin-fluctuation mechanism proposed is Abrikosov-Gor'kov Cooper-pair breaking by Pr.[14,19–23] (In general, the theories have not provided a clear and convincing explanation of exactly how rare-earth-site Pr supposedly breaks pairs, while other magnetic ions on rare-earth sites do not; indeed, in the case of $PrBa_2Cu_3O_7$, an indirect pair breaking due to "hybridization" is often invoked,[24] despite considerable experimental evidence to the contrary.) *Both the charge-fluctuation and the spin-fluctuation explanations are embedded in a theoretical framework that locates the root of superconductivity in the* $[CuO_2]^{-2}$ *cuprate planes.* (See Fig. 1.)



(a) $PrBa_2Cu_3O_7$ (b) $Pr_2Ba_4Cu_8O_{16}$

FIG. 1. Crystal structure of (a) $PrBa_2Cu_3O_7$ and (b) $PrBa_2Cu_4O_8$, the double-chain-layer compound. The legend is on the figure. Note that the unit cell for (b) is twice as large as the formula unit, with chemical composition $Pr_2Ba_4Cu_8O_{16}$.

The charge-fluctuation mechanisms must also deal with the issues raised by an actinide *nonsuperconductor:* $CmBa_2Cu_3O_x$ with $x \approx 7$,[14] which is isostructural to both insulating $PrBa_2Cu_3O_x$ and superconducting $GdBa_2Cu_3O_x$. Cm has almost the same electronic structure as Gd (Cm^{+3} has a Rn core plus seven $5f$ electrons, while Gd has a Xe core with seven $4f$ electrons), and appears to be in the Cm^{+3} valence state in $CmBa_2Cu_3O_x$, but does not superconduct.[14] Thus, even if Pr is in the Pr^{+4} state in $PrBa_2Cu_3O_x$, the nonsuperconducting nature of $CmBa_2Cu_3O_x$ apparently must be explained without charge fluctuations to the $+4$ state, which seem to be unnecessary for quenching superconductivity. Furthermore Tb is reported by some authors[7] to assume the Tb^{+4} state in $Y_{1-y}Tb_yBa_2Cu_3O_x$, but Tb doping does *not* degrade the superconductivity,[7] suggesting that the presence of $+4$ ions is not sufficient to destroy superconductivity either. Thus charge fluctuations as normally invoked appear to be neither necessary nor sufficient for quenching superconductivity.

The spin-fluctuation models have comparable problems with the data for the double-chain-layer materials $YBa_2Cu_4O_y$ with $x \approx 8$. These materials have 15 atoms per formula unit, with one extra atom each of Cu and O forming a second chain (relative to single-chain $YBa_2Cu_3O_x$ with $x \approx 7$), with the new chain axis parallel to the first chain axis, but displaced relative to it (Fig. 1). (The formula unit corresponds to only half of a unit cell of double-chain material, as shown in Fig. 1.) The formula unit is slightly larger than for single-chain material, the superconducting transition temperature is almost the same (≈ 90 K versus ≈ 84 K), and the number of holes per formula unit is the same (implying that the Fermi energies of the two materials are comparable). Therefore, if the superconducting characters of $YBa_2Cu_3O_x$ and its homologous isostructural compounds are governed both by the cuprate planes and by the holes that migrate to those planes from the chains, and if magnetic interactions in $PrBa_2Cu_3O_x$ (involving the holes in the planes and the magnetic moments of dopant Pr ions) quench the superconductivity, subsequently leading to the insulating character of $PrBa_2Cu_3O_x$, then the breakdown of superconductivity in $Y_{1-y}Pr_yBa_2Cu_3O_x$ with $x \approx 7$ and $Y_{1-y}Pr_yBa_2Cu_4O_x$ with $x \approx 8$ should set in at approximately the same critical Pr contents y_c. The fact that they do not (y_c of 0.3 to 0.5 for single-layer material[20,21,25,26] versus 0.75 to 0.9 for double layers[27–29]) implies that the spin fluctuations which determine the magnetic properties (magnetic moment of Pr, Pauli paramagnetism) are different from the determinants of the superconducting properties.[29]

Another fact difficult to reconcile with a spin-fluctuation model is the Tokura-Torrance[30] empirical rule for the phase boundary between superconducting and insulating $YBa_{2-v}La_vCu_3O_x$ with $x \approx 7$: $x = 6.5 + v$. Only a very complicated spin-fluctuation theory could produce such a simple rule for the effects of nonmagnetic La^{+3}. (In contrast, the oxygen model attributes the Tokura-Torrance rule to passivation of La by oxygen.[15,16,18])

Neither the charge-fluctuation models nor the conventional spin-fluctuation models are consistent with these very basic data. Here we offer a much simpler explanation of the data: (i) The superconductivity originates in the chain layers, not in the $[CuO_2]^{-2}$ cuprate planes.[15,16,18] (ii) Some Pr ions occupy Ba sites,[31,32] where they break Cooper pairs in the adjacent Cu-O chain layers according to the Abrikosov-Gor'kov theory for exchange scattering of Fermi-energy carriers by magnetic ions. (iii) The large *size* of Pr^{+3} is the unique feature which leads to its bonding and higher solubility at a Ba site: the Ba^{+2} ion replaced by the Pr^{+3} is very large (1.42 Å vs 1.13 Å), and so only the largest rare-earth ions have small enough size mismatches to achieve appreciable solubility at Ba sites.[33–35]

II. EVIDENCE FOR THE ROLE OF Ba-SITE Pr

The experimental evidence supporting this viewpoint is compelling: all of the explanation's major elements have been proven to be true.

A. Superconductivity in the chains

Until recently, it has been widely *assumed* that high-temperature superconductivity invariably originates from cuprate planes, which are common to most (but not all) high-temperature superconducting materials. This thinking has changed recently, as a result of several demonstrations that the superconductivity originates from dopant oxygen, usually in "charge-reservoir" layers. The charge-reservoir regions of $YBa_2Cu_3O_x$ and its homologues are the chain layers, where the dopant oxygen resides [Fig. 1(a)].

Some of the evidence for superconductivity originating in the chain layers (rather than in cuprate planes) includes: Magnetic ions on the rare-earth sites in (rare-earth)$Ba_2Cu_3O_x$ do not destroy superconductivity,[1] because they are remote from the chain layers in which the superconductivity is rooted;[15–18,36,37] but the same ions on Ba sites do disrupt superconductivity, because the adjacent chain layers (which contain the dopant oxygen) are the root of superconductivity, and are near enough for Cooper pair breaking to occur via short-ranged exchange scattering. Indeed, the cases of pair breaking by Ba-site Nd in $Nd_{1+u}Ba_{2-u}Cu_3O_x$ and Ba-site Gd in $Gd_{1+u}Ba_{2-u}Cu_3O_x$ are now well documented,[17,38] and show that the superconductivity is rooted in the charge-reservoir chain layers, rather than in the cuprate planes. Studies of hole localization in the $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4+\delta}$ and $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ compounds (for $n = 1,2,\ldots$) also show that the charge-reservoir regions containing the dopant (interstitial) oxygen are the root of the superconductivity, not the cuprate planes.[36] (These charge-reservoir regions are analogous to the chain layers of $YBa_2Cu_3O_x$.) Moreover, the superconductivity observed in the La_2CuO_4-based and Nd_2CuO_4-based materials has been shown to come from the charge-reservoir vicinity of the interstitial dopant oxygen atoms, not from the cuprate planes.[37] Finally, the system $Ba_{1-a}K_aPb_{1-b}Bi_bO_x$ with $x \approx 3$ has no cuprate planes, but does have dopant (substitutional) oxygen, and does produce high-temperature superconductivity.[39]

Direct observation of superconductivity in the dopant-oxygen Bi-O layers of $Bi_2Sr_2CaCu_2O_x$ with $x \approx 8$ (BSCCO) has been reported recently by Wolf *et al.*[40] This observation, combined with experiments measuring the critical current as a function of magnetic field and determining the spectrum of Josephson radiation induced by current injected along the *c* axis of BSCCO, shows that there is only one superconducting slab per formula unit, and so demonstrates that the cuprate planes of BSCCO are insulating while the dopant-oxygen layers superconduct.[41,42]

The observed pair-breaking behavior[20–22,43] of Pr in $Y_{1-y}Pr_yBa_2Cu_3O_x$ is clearly associated with the local moments of Pr ions. It cannot be credibly assigned to $J=4$ Pr^{+3} on the Y or rare-earth site, however, because no other $(\text{rare-earth})^{+3}$ ion on the rare-earth site, even large-spin Ho^{+3} ($J=8$), destroys the superconductivity. Assignment to $J=5/2$ Pr^{+4} (Refs. 44 and 45) would require some complex interaction between the local moment and the $+4$ charge state, would strain credibility, and so is also considered inappropriate. If the Pr moments are responsible for destroying the superconductivity, and if rare-earth-site Pr ions are not, then the Pr must occupy another site when it breaks Cooper pairs, and that site must be near the origin of superconductivity. Examination of the crystal structure reveals that the only cation site large enough to accommodate Pr^{+3} is a Ba site and that chain-O must therefore be the origin of superconductivity.

The main reason that the observations in $Y_{1-y}Pr_yBa_2Cu_3O_x$ have not been assigned previously to pair breaking by Ba-site Pr is the incorrect *assumption,* based on the charge-transfer hypothesis[46] (now known to be invalid), that the superconductivity is rooted in the cuprate planes. This assumption is necessarily followed by intellectual gymnastics to explain why magnetic ions on rare-earth sites do *not* break pairs—gymnastics which imply that Ba-site magnetic ions do not break pairs either (because the Ba site and the rare-earth site are comparably close to the cuprate planes, and have similar environments).[47] Recognition that the superconductivity is rooted in the chain layers explains why rare-earth-site magnetic ions do not break pairs (they are remote from the chain layers), while Ba-site magnetic ions do (they are adjacent to the superconducting chains). Ba-site Pr^{+3} ions scatter holes in the adjacent chain layers, breaking Cooper pairs and disrupting superconductivity.

B. Ba-site Pr

There is no dispute about whether Pr is present on some Ba sites. The chemistry of sample preparation and x-ray data[31,48] both lead to the conclusion that there must be some Ba-site Pr in $PrBa_2Cu_3O_x$—namely, that the material is actually $PrBa_{2-u}Pr_uCu_3O_x$, with *u* being significant[14,17] [values of $u \sim 0.5$ have been reported for $Nd_{1+u}Ba_{2-u}Cu_3O_x$ (Ref. 49)]. The ordinary neutron-scattering data are insensitive to the difference between Ba and Pr,[50] but nevertheless reveal significant occupancy of the antichain or O(5) site by oxygen (7%),[32] which is a signature of an ion on the adjacent Ba site in the $+3$ valence state: Nd^{+3} and La^{+3} are known to be correlated with antichain oxygen when they occupy Ba sites.[49–52] The antichain site is in the Cu-O chain layers, in between chain-Cu atoms on the *a* axis of Fig. 1(a), and is normally empty in $PrBa_2Cu_3O_x$ and its homologues. Thus the antichain oxygen of $PrBa_2Cu_3O_x$ indicates the presence of Ba-site Pr^{+3}. Magic-angle spinning nuclear magnetic resonance studies have also detected Ba-site Pr,[53] as have spin-polarized neutron-scattering experiments.[54] Thus chemical analyses, x-ray data, ordinary neutron scattering, nuclear magnetic resonance, and spin-polarized neutron scattering all lead to the same conclusion: clearly Ba-site Pr is present in materials such as $Y_{1-y}Pr_yBa_2Cu_3O_x$.

C. The role of ionic size

In this picture, the magnetic rare-earth ions Ce^{+3} and Pr^{+3} are unique because of their large sizes, which allow them to occupy Ba sites without too much lattice distortion. The actinide Cm^{+3} is also comparably large,[55] and so $CmBa_2Cu_3O_x$ with $x \approx 7$ is nonsuperconducting, much as $PrBa_2Cu_3O_x$ is. Considerably smaller ions would have difficulty occupying a Ba site in the (rare-earth)-$Ba_2Cu_3O_x$ structure, being too small to efficiently bond to the site's neighbors. La^{+3}, while larger in radius than Ce^{+3} or Pr^{+3}, is nonmagnetic ($J=0$), and so, while La^{+3} does occupy Ba sites, it does not exchange scatter and break pairs. Hence $LaBa_2Cu_3O_x$ is superconducting at ≈ 90 K, not insulating.[56] Nd^{+3}, the next largest $(\text{rare-earth})^{+3}$ ion after La^{+3}, Ce^{+3}, and Pr^{+3}, does occupy Ba sites, does break pairs, and does quench superconductivity.[17,49] The rare-earth ions larger than Nd^{+3} should do likewise.

D. The importance of rare-earth occupancy of Ba sites

While almost all rare-earth ions are magnetic, they break pairs only when they are adjacent to the primary superconducting layers, which are the *chain* layers. Such pair breaking is significant only if a significant concentration of rare-earth ions occupy Ba sites, and so the *solubility* of the rare earth at a Ba site is the determining factor for pair breaking and the quenching of superconductivity. Thus only the *large, magnetic* rare-earth (and actinide) ions, which can replace very large Ba^{+2}, break pairs and quench superconductivity. Such pair breaking in the (rare-earth)$Ba_2Cu_3O_x$ class of materials is extrinsic, not intrinsic, and is controlled by native defects, such as Pr ions on Ba sites. Indeed, the fact that the critical composition y_c of $Y_{1-y}Pr_yBa_2Cu_3O_x$ is different for different materials-processing schemes[20,21,25–29] indicates that a defect determines the effect.

III. EVIDENCE FROM DOUBLE-CHAIN-LAYER $Y_{1-y}Pr_yBa_2Cu_4O_x$ WITH $x \approx 8$

The double-chain-layer system (Fig. 1) $Y_{1-y}Pr_yBa_2Cu_4O_x$ with $x \approx 8$, when compared with the single-layer material $Y_{1-y}Pr_yBa_2Cu_3O_x$ with $x \approx 7$, provides strong evidence for the Ba-site Pr model. The single- and double-layer materials for $y = 0$ have almost the same superconducting transition temperatures (≈ 90 K versus ≈ 84 K). But quenching the superconductivity in *both* chain layers requires pair breaking Pr on Ba sites on *both* sides of a particular double-chain layer—implying that the critical composition y_c of Pr ions for totally quenching the superconductivity in the double-chain-layer system must be larger than for the single-layer system (almost twice as large), which it is: 0.9 versus 0.5 (Refs. 20, 21, 25, 27, and 29). In contrast, a cuprate-plane model (as discussed above) implies that y_c is about the same for single- and double-chain materials, because the chains are supposedly part of a relatively inert charge reservoir that merely "dopes the planes" with holes.

IV. $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_x$ WITH $x \approx 7$

One spectacular consequence of this picture[15–18] with Ba-site rare-earth ions destroying the superconductivity is that $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_x$ with $x \approx 7$ is expected to superconduct although $Y_{0.5}Pr_{0.5}Ba_2Cu_3O_x$ does not, being at the limit for which T_c vanishes: $Y_{0.5}Pr_{0.5}Ba_2Cu_3O_x$ has just enough Ba-site Pr to quench its superconductivity.[20,21,26] In contrast, $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_x$ should have fewer Ba-site Pr ions, because Ca^{+2} is almost the same size as Pr^{+3}, and so competes with Pr for Ba-site occupancy, while Y^{+3} is too small to compete effectively.[33] In fact, $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_x$ *films* with $x \approx 7$ do superconduct[57] with a critical temperature of 43 K. We interpret this as meaning that there is enough Ba-site Pr in the films to reduce T_c to about half of 90 K, the value for ideal (rare-earth) $Ba_2Cu_3O_7$.

Hole-filling by Pr^{+4} does not explain the 43 K superconductivity of the $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_x$ films, which would have a transition temperature of ≈ 90 K if the deviations from $+3$ of the charges of rare-earth-site Pr^{+4} and Ca^{+2} compensated one another. Moreover, Norton *et al.* observed a dramatic dependence of the critical temperature on the *substrate temperature* of their films: the lowest substrate temperatures yield the highest superconducting critical temperatures. While substrate temperature will certainly affect site occupancies, including occupancy of Ba sites by Pr, it is difficult to imagine how it would greatly alter the charge- or spin-fluctuation spectrum. Sample thickness also affects the superconductivity, again indicating the importance of growth kinetics capable of occupying Ba sites with Pr: *bulk* samples of $Pr_{0.5}Ca_{0.5}Ba_2Cu_3O_x$ prepared by Norton *et al.* do *not* superconduct.

V. OTHER CONSEQUENCES

Li, Chen, and Qian[58] have shown that $LaBaPrCu_3O_{7.36}$ is a semiconductor, while $LaBaCaCu_3O_{7-\delta}$ superconducts. Those authors assume that La ions occupy Ba sites, and that Pr is restricted to rare-earth sites. In reality, Pr almost certainly occupies Ba sites in sufficient concentrations to quench the superconductivity of $LaBaPrCu_3O_{7.36}$. We predict that neutron-scattering measurements on these materials will reveal Pr on the Ba sites. In this regard, we note that Pr on a Ba site is very difficult to discriminate from Ba in neutron scattering:[50] samples prepared with isotopically enriched $^{137}Ba/^{138}Ba$ ratios may be required to detect Pr in a Ba background. However, Ca can be discriminated from Ba, and so the combination of neutron scattering plus very careful chemical analyses should be able to determine the site occupancies of La, Ca, and Pr in these materials.

Other observations that can be easily understood with the present model are (i) $La_{1-y}Pr_yCaBaCu_3O_{7-\delta}$ superconducts for $y < 0.6$,[48] the superconductivity being quenched when Pr, which occupies both the rare earth and the Ba sites of this material, accumulates in sufficient concentration on the Ba sites. (ii) $PrBa_{2-y}Ca_yCu_3O_{7-\delta}$ does not superconduct[48] because of Pr on Ba sites. [Further doping of this material with Pr is known to increase the resistivity, associated with Ba-site Pr (Ref. 48).] (iii) $Pr_{0.8}Ca_{0.2}Ba_2Cu_3O_x$ with $x = 6.9$ or 6.08 does not superconduct,[48] because it contains too much Ba-site Pr, and perhaps also because it does not contain enough Ca^{+2} to compensate for any Pr^{+4} and to create the undercharged oxygen needed for superconductivity.[15,16,18]

The present work adds a third type of mechanism for explaining $Y_{1-y}Pr_yBa_2Cu_3O_x$ data, and so may require revision of some of the conclusions of earlier work. For example, the beautiful studies of $Y_{1-y-u}Pr_yCa_uBa_2Cu_3O_x$ (Ref. 44) may need to be reinterpreted in terms of Ba-site Pr as well as hole filling and pair breaking, but nevertheless still provide an important description of $T_c(u,y)$.

Our viewpoint is that the magnetic moment of a Pr ion on a Ba site breaks Cooper pairs and locally destroys the pairing correlations essential to superconductivity. Once these correlations are broken, Coulomb interactions[59] become dominant and drive the materials toward the insulating state, a situation that may be facilitated by shallow traps associated with Ba-site Pr.

VI. NÉEL TEMPERATURES

An interesting and perplexing fact has been that $PrBa_2Cu_3O_x$ and $CmBa_2Cu_3O_x$ with $x \approx 7$ both have very high antiferromagnetic ordering temperatures: 17 and 22 K,[14] an order of magnitude higher than for other (rare-earth)$Ba_2Cu_3O_x$ materials. This is probably due to the Ba-site Pr, which, in addition to the rare-earth-site Pr, produces the antiferromagnetism. The Ba-site Pr effectively bridges between the rare-earth sites, making the antiferromagnetism effectively stronger, and increasing the Néel temperature.

VII. VALENCE OF Pr

There has been a raging controversy for years concerning the valence of Pr in this class of materials: is it Pr^{+4}, Pr^{+3}, or a mixture of the two? Many data taken under high vacuum, or with surface-sensitive probes, or with heating probes have reported Pr^{+3}.[14,60–69] Bulk probes such as magnetic susceptibility, Hall effect, and specific heat tend to favor Pr^{+4} (on the rare-earth site) or a combination of Pr^{+3} and Pr^{+4},[8–10,20,34,35,44,57,70,71] as do our own analyses of neutron-diffraction data (see below). We believe that this difference is sometimes related to the oxygen in the samples, which may leak out of the surface under certain conditions, leaving more Pr^{+3} in the sample than Pr^{+4}. Clearly, if all of the oxygen is ionic O^{-2} (which it may not be), then we expect insulating ideal $PrBa_2Cu_3O_7$ to have Pr^{+4}, Cu^{+2}, and Ba^{+2} to satisfy valence rules. However, $YBa_2Cu_3O_7$ almost certainly has its Y in the Y^{+3} charge state, and there is no evidence of Cu^{+3},[72] and so not all of the O can be fully ionized to O^{-2} in $YBa_2Cu_3O_7$ (and by inference also in $PrBa_2Cu_3O_7$) if charge is balanced as it must be. Therefore any analysis of ionic charges must allow for some undercharged oxygen. Nevertheless we shall determine (see below) from the neutron data that the oxygen atoms appear to be primarily in the O^{-2} ionic state. If all oxygen is O^{-2}, then Pr must be Pr^{+4} in order to balance charge in the unit cell of $PrBa_2Cu_3O_7$. Similarly ideal $PrBa_2Cu_3O_6$ will have chain oxygen in the Cu^{+1} state, Pr in the Pr^{+3} state, and oxygen ionized to O^{-2}.

An examination of the magnitudes of the Madelung potentials (33.3 V on the rare-earth site and 17.0 V on the Ba site[73]) and work functions [~4 to 5 V (Ref. 74)] of (rare-earth)$Ba_2Cu_3O_7$ compounds, in comparison with rare-earth ionization potential [~21.6 V and ~39.0 V to ionize Pr^{+2} and Pr^{+3} (Ref. 3)] indicates that on the Ba site we have Pr^{+3}, while Pr on the rare-earth site is within ~1.7 V of undergoing the reaction $Pr^{+3} \rightarrow Pr^{+4} + e^-$. The uncertainties in the theoretical potentials are large enough to permit one to believe that Pr is either Pr^{+4} or Pr^{+3} on the rare-earth site. We do note however that the presence of Pr on a Ba site alters the Madelung potential and reduces the likelihood that nearby rare-earth-site Pr is the Pr^{+4} charge state. Thus, it is not unreasonable to assume that both Pr^{+4} and Pr^{+3} are present on the rare-earth sites in actual materials.

To a great degree, the present model renders the valence controversy moot, by noting that Pr^{+3} *on a Ba site* breaks pairs and destroys the superconductivity. Hence the valence of rare-earth-site Pr is not highly relevant to the issue of superconductivity.

Nevertheless, we have analyzed the neutron-scattering data and have extracted the charges on each of the ions in $Y_{1-y}Pr_yBa_2Cu_3O_x$ with $x \approx 7$, as the Pr content y varies from zero to unity. We use the empirical bond-valence-sum method,[75] which determines effective charges on each of the ions from the totality of its nearest-neighbor bond lengths. This is a well-established method of chemistry, which represents a quantification of Pauling's ideas about chemical bonds,[76] and can be expected to produce correct charges to within $\pm 0.1|e|$, where e is the electron's charge. Indeed, the method can be run backwards. Instead of having bond lengths as input and charges as output, one can input the classical valence charges of each of the ions ($+2|e|$ for Ba, etc.) and then compute the crystal structure. We have done that for $YBa_2Cu_3O_{6.5}$, and have found a tetragonal structure with the a and b axes about 6% longer, and the c axis about 8% shorter than the experimental structure.[16] This calculation gives us confidence in the method run forwards. The results of the bond-valence-sum analyses are interesting [Figs. 2 and 3 (Ref. 32)].

The oxygen sites (Fig. 2) all have charges near $-2|e|$, with the chain oxygen's charge being almost independent of Pr doping. The Ba-O layer's bridging oxygen transfers about $0.1|e|$ to the planes as the Pr content increases from zero to unity and the bridging oxygen moves toward the cuprate planes. The oxygen ions in the cuprate planes appear to become slightly more negative as the Pr is added, because the Pr's $4f$ electron participates in bonds with them. [The nearer plane oxygen O(2), is, not surprisingly, affected by the Pr slightly more.]

The rare-earth site (Fig. 3) increases its charge by about $0.5|e|$ as the Pr content y increases from zero to unity—a clear signature that some or all of the Pr on that site is in the Pr^{+4} state. About half of the extra electron from Pr goes onto the adjacent cuprate planes, with about half remaining on or near the Pr. (The method does *not* permit us to determine if *every* Pr or an *average* Pr has this charge distribution.) Thus, to a good approximation, the extra electron does not reach the chain layers. Finally, the Cu and Ba sites have almost constant charges.

The detection of significant amounts of Pr^{+4}, as indicated by our analyses of the neutron diffraction data, implies that rare-earth-site Ce or Pr cannot be responsible for the observed pair breaking: If Pr is ionized to Pr^{+4}, then Ce on the same site, having a lower ionization potential, will also be Ce^{+4}. But Ce^{+4} is a closed-shell non-

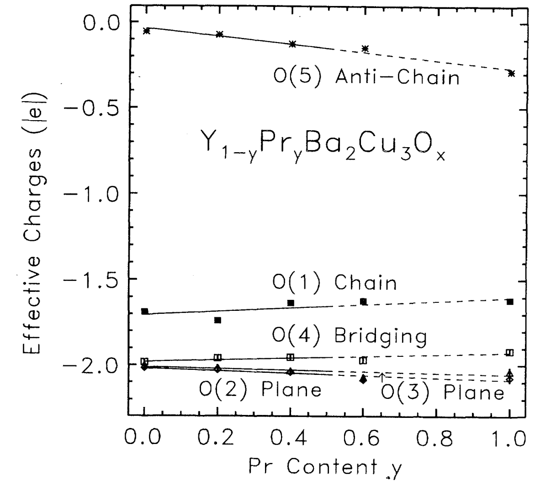


FIG. 2. Bond-valence-sum charges of the oxygen sites versus Pr content y in $Y_{1-y}Pr_yBa_2Cu_3O_x$ with $x \approx 7$, as extracted from the Rietveld-refined neutron data of Ref. 32. Note that chain oxygen (filled squares) maintains an almost constant charge, as does bridging oxygen in the Ba-O plane (open squares), and the two cuprate-plane oxygens O(3) (triangles) and O(2) (diamonds). Oxygen at the antichain O(5) site (asterisks) gains charge with Pr content, which actually reflects primarily increased occupancy of that site by charged oxygen. The solid (dashed) line represent fits to the data for superconducting (nonsuperconducting) material.

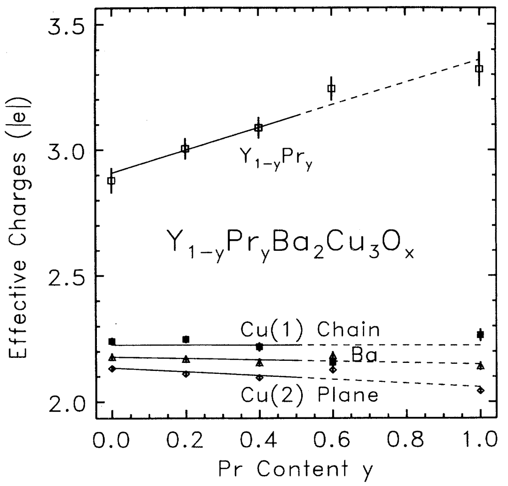


FIG. 3. Bond-valence-sum charges of the cation sites versus Pr content y in $Y_{1-y}Pr_yBa_2Cu_3O_x$ with $x \approx 7$, as extracted from the Rietveld-refined neutron data of Ref. 32. Note that as the Pr content y increases from zero to unity, the rare-earth-site $Y_{1-y}Pr_y$ charge (open squares) increases by $\approx 0.5|e|$, indicating that at least some of the Pr is in the Pr^{+4} state. The solid (dashed) line represents fits to the data for superconducting (nonsuperconducting) material. The chain-Cu (filled squares), Ba (triangles), and cuprate-plane-Cu (diamonds) sites have charges that are relatively independent of y.

magnetic ion, and so cannot break pairs through the exchange interaction. Since the pair breaking of Pr is so similar to that of Ce, and since both pair breaking effects scale with the Pr or Ce content, it follows that the observed pair breaking is caused by Pr or Ce that does not occupy a rare-earth site.

If one chooses to ignore all of the evidence for Ba-site Pr, then he must explain (i) why only Pr and Ce break pairs and degrade the superconductivity, when the other rare-earth ions do not; and (ii) why Nd on a Nd site in $NdBa_2Cu_3O_x$ does not break pairs, but Ba-site Nd does.[17]

VIII. SUMMARY

In summary, by placing some Pr ions on Ba sites, where they break Cooper pairs in the adjacent chain layers, we can easily understand why $PrBa_2Cu_3O_7$ is not a superconductor. In fact, this picture allows us to sort out many previously unexplained data for $Y_{1-y}Pr_yBa_2Cu_3O_x$ and related materials. We hope that experiments quantitatively correlating Ba-site occupancy with degraded superconductivity will confirm the picture.

Note added in proof. We have recently observed superconductivity in $PrBa_2Cu_3O_7$, confirming the physical picture presented in this paper and in Ref. 17.

ACKNOWLEDGMENTS

We are grateful to the U.S. Air Force Office of Scientific Research, the U.S. Army Research Office, the U.S. Office of Naval Research, and the U.S. Department of Energy for their financial support of this work (Contracts No. AFOSR-F49620-94-10163, DAAL03-91-G-0054, N00014-94-10147, and DE-FG02-90ER45427), to D. Pulling for technical support, and to F. Mueller and W. B. Yelon for stimulating discussions.

---

[1] Z. Fisk, J. D. Thompson, E. Zirngiebl, J. L. Smith, and S. W. Cheong, Solid State Commun. **62**, 743 (1987); P. 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).

[2] For a review, see H. B. Radousky, J. Mater. Res. **7**, 1917 (1992); and Ref. 6.

[3] U. Staub, M. R. Antonio, J. S. Xue, L. Soderholm, C. K. Loong, M. Guillaume, and A. Furrer, Bull. Am. Phys. Soc. **39**, 67 (1994); and U. Staub (private communication). Tb is partially soluble on the Y site of $YBa_2Cu_3O_x$, but not very soluble on the Ba site. Y-site Tb does not depress T_c at all significantly. Beyond its limits of solubility, Tb forms $TbBaO_3$, with valence Tb^{+4}. Ce also forms a similar compound, $CeBaO_3$, but unlike Tb, both Ce and Pr are rather soluble on the Ba site.

[4] Ce, Pr, and Tb, in that order, are the three rare earths most easily ionized to the +4 state (Ref. 5).

[5] *Chemical Rubber Company Handbook*, 74th ed., edited by D. R. Lide (Chemical Rubber, Bombay, 1993-1994), p. 10-205.

[6] C. R. Fincher, Jr. and G. B. Blanchet, Phys. Rev. Lett. **67**, 2902 (1991).

[7] G. Cao, R. J. Kennedy, J. W. O'Reilly, J. E. Crow, P. Pernambuco-Wise, and S. T. Ting, Physica B **186-188**, 1022 (1993).

[8] L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgensen, C. U. Segre, and I. K. Schuller, Nature (London) **328**, 604 (1987).

[9] J. K. Liang, T. Xu, S. S. Xie, G. H. Rao, X. Y. Shao, and Z. G. Dian, Z. Phys. B **69**, 137 (1987).

[10] 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).

[11] A. Kebede, C.-S. Jee, J. Schwegler, J. E. Crow, T. Mihalisin, G. H. Myer, R. E. Salomon, P. Shlottmann, M. V. Kuric, S. H. Bloom, and R. P. Guertin, Phys. Rev. B **40**, 4453 (1989).

[12] J. L. Peng, P. Klavins, R. N. Shelton, H. B. Radousky, B. A. Hahn, and L. Bernardez, Phys. Rev. B **40**, 4517 (1989).

[13] G. Cao, J. Bolivar, J. W. O'Reilly, J. E. Crow, R. J. Kennedy, and P. Pernambuco-Wise, Physica B **186-188**, 1004 (1993).

[14] L. Soderholm, G. L. Goodman, U. Welp, C. W. Williams, and J. Bolender, Physica C **161**, 252 (1989).

[15] H. A. Blackstead and J. D. Dow, Pis'ma Zh. Eksp. Teor. Fiz. **59**, 262 (1994) [JETP Lett. **59**, 283 (1994)], and references therein; Proc. SPIE (to be published); J. Superconduct. (to be published); and (unpublished).

[16] H. A. Blackstead and J. D. Dow (unpublished). This work on oxide superconductivity achieves suprconductivity by Cooper-pairing holes through the polarization field. Two main parts of the polarization field are soft-mode pairing (strong coupling) and excitonic pairing *via* $2h^{+}+O^{-2} \rightarrow O^{0}$ (weak coupling).

[17] H. A. Blackstead, J. D. Dow, W. E. Packard, and D. B. Pul-

ling, Physica C **235-240**, 1363 (1994); H. A. Blackstead, D. B. Chrisey, J. D. Dow, J. S. Horwitz, A. E. Klunzinger, and D. B. Pulling, *ibid.* **235-240**, 1539 (1994); H. A. Blackstead and J. D. Dow, J. Supercond. (to be published); H. A. Blackstead, J. D. Dow, J. F. Federici, W. E. Packard, and D. B. Pulling, Physica C **235-240**, 2161 (1994); H. A. Blackstead and J. D. Dow (unpublished).

[18] H. A. Blackstead and J. D. Dow, in *Proceedings of the Second International Symposium on Quantum Confinement Physics and Applications,* edited by M. Cahay, S. Bandyopadhyay, J. P. Leburton, A. W. Kleinsasser, and M. A. Osman (Electrochemical Society, Pennington, NJ, 1994), Vol. 94-17, pp. 408, 419.

[19] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)]. Pair breaking is often also accompanied by bell-shaped upper-critical field curves (Refs. 14 and 22).

[20] C.-S. Jee, A. Kebede, D. Nichols, J. E. Crow, T. Mihalisin, G. H. Myer, I. Perez, R. E. Salomon, and P. Schlottmann, Solid State Commun. **69**, 379 (1989).

[21] J. L. Peng, P. Klavins, R. N. Shelton, H. B. Radousky, B. A. Hahn, and L. Bernardez, Phys. Rev. B **40**, 4517 (1989).

[22] S. K. Malik, C. V. Tomy, and P. Bhargava, Phys. Rev. B **44**, 7042 (1991). The pair breaking is accompanied by the characteristic bell-shaped upper-critical field curve H_{c2}.

[23] Y. Xu and W. Guan, Solid State Commun. **80**, 105 (1991); Appl. Phys. Lett. **59**, 2183 (1991); Physica C **183**, 105 (1991).

[24] R. Fehrenbacher and T. M. Rice, Phys. Rev. Lett. **70**, 3471 (1993).

[25] K. Koyama, Y. Suzuki, and S. Noguchi, Jpn. J. Appl. Phys. **27**, 1862 (1988).

[26] B. Okai, M. Kosuge, H. Nozaki, K. Takahashi, and M. Ohta, Jpn. J. Appl. Phys. **27**, L41 (1988).

[27] K. Koyama, S. Taga, and S. Noguchi, Physica C **185-189**, 771 (1991).

[28] A. P. Litvinchuk, C. Thomsen, M. Cardona, L. Börjesson, M. Käll, P. Berastegui, and L. G. Johansson, J. Supercond. **7**, 113 (1994).

[29] N. Yamada, Z. Guo, N. Ikeda, K. Kohn, T. Iri, and K. I. Gondaira, Physica C **185-189**, 809 (1991).

[30] Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, Phys. Rev. B **38**, 7156 (1988).

[31] P. Karen, H. Fjellvag, O. Braaten, A. Kjekshus, and H. Bratsberg, Acta Chem. Scand. **44**, 994 (1990).

[32] J. J. Neumeier, T. Bjornholm, M. B. Maple, J. J. Rhyne, and J. A. Gotaas, Physica C **166**, 191 (1990).

[33] Eightfold-coordinated Ba^{+2} has an ionic radius of 1.42 Å, while Pr^{+3} had a radius of 1.13 Å, almost the same as Ca^{+2}'s (1.12 Å), which is known to readily replace Ba^{+2} (suggesting that an ionic radius of 1.12 Å is large enough for bonding). Note that on this scale Y^{+3} has a radius of 1.02, almost the same as that of Pr^{+4} (Ref. 34). Except for nonmagnetic ($J=0$) La^{+3} with radius 1.16 Å (which would not pair break by exchange scattering) and magnetic ($J=5/2$) Ce^{+3} (radius 1.14 Å) which is known to depress T_c much as Pr does (Ref. 6), Pr is the largest (rare earth)$^{+3}$ ion. Smaller ions should be less soluble at the Ba site because of the size mismatch.

[34] A. Kebede, C.-S. Jee, J. Schwegler, J. E. Crow, T. Mihalisin, G. H. Myer, R. E. Salomon, P. Shlottmann, M. V. Kuric, S. H. Bloom, and R. P. Guertin, Phys. Rev. B **40**, 4453 (1989); see also Ref. 35.

[35] A. P. Reyes, D. E. McLaughlin, M. Takigawa, P. C. Hammel, R. H. Heffner, J. D. Thompson, J. E. Crow, A. Kebede, T. Mihalisin, and J. Schwegler, Phys. Rev. B **42**, 2688 (1990); A. P. Reyes, D. E. McLaughlin, M. Takigawa, P. C. Hammel, R. H. Heffner, J. D. Thompson, and J. E. Crow, *ibid.* **43**, 2989 (1991); see also Ref. 20.

[36] H. A. Blackstead and J. D. Dow (unpublished).

[37] H. A. Blackstead and J. D. Dow, Superlatt. Microstruct. **14**, 231 (1993); Philos. Mag. (to be published).

[38] V. N. Narozhnyi, E. P. Khlybeb, V. I. Nizhankovskii, and Z. Bukowski, *Proceedings of the XXIX Conference on Low-Temperature Physics* (Kazan, 1992), Pt. 1, p. 2.

[39] R. G. Goodrich, C. Grienier, D. Hall, A. Lacerda, E. G. Haanappel, D. Rickel, T. Northington, R. Schwarz, F. M. Mueller, D. D. Loelling, J. Vuillemin, L. Van Bockstal, M. L. Norton, and D. H. Lowndes, J. Phys. Chem. Solids **54**, 1251 (1993).

[40] E. L. Wolf, A. Chang. Z. Y. Rong, Yu. M. Ivanchenko, and F. Lu, J. Supercond. **7**, 355 (1994).

[41] R. Kleiner and P. Müller, Phys. Rev. B **49**, 1327 (1994).

[42] The interpretations in Refs. 40 and 41 are mutually incompatible, however, because superconductivity in both the Bi-O layers and the cuprate planes implies *two* Josephson junctions per formula unit, not one.

[43] The degradation of the superconductivity in (rare-earth) Ba$_2$Cu$_3$O$_x$ systems by Ce, Pr, Nd, Cm, and Gd, all of which are magnetic ($J \neq 0$) in the $+3$ charge state, but not by nonmagnetic ($J=0$) La, proves the magnetic character of the degradation. (The local Madelung potential will ionize these ions, in an antichain-oxygen environment, to the $+3$ charge state.)

[44] J. J. Neumeier, T. Bjørnholm, M. B. Maple, and I. K. Schuller, Phys. Rev. Lett. **63**, 2516 (1989).

[45] Recall that the degradation of the superconductivity is due to the *magnetic moment,* not the charge state of the Pr (Ref. 43).

[46] R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck, Jr., and L. W. Rupp, Jr., Physica C **165**, 419 (1990).

[47] A. J. Freeman (private communication) and co-workers have argued that the local-state density at the Fermi energy is so low near the rare-earth site that the site is effectively magnetically isolated from the Fermi sea. However, the spin relaxation on that site is Korringa-like (indicating efficient coupling to the Fermi liquid), and the state density at the Ba site is comparably low—and Nd on a Ba site certainly breaks pairs in NdBa$_2$Cu$_3$O$_x$. See A. J. Freeman, J. Yu, S. Massidda, and D. D. Koelling, Phys. Lett. A **122**, 198 (1987); J. T. Markert, T. W. Noh, S. E. Russek, and R. M. Cotts, Solid State Commun. **63**, 847 (1987); and Ref. 17.

[48] C. Infante, M. K. El Mously, R. Dayal, M. Husain, S. A. Siddiqi, and P. Ganguly, Physica C **167**, 640 (1990).

[49] M. J. Kramer, S. I. Yoo, R. W. McCallum, W. B. Yelon, H. Xie, and P. Allenspach, Physica C **219**, 145 (1994).

[50] W. B. Yelon (private communication).

[51] P. R. Slater and C. Greaves, Supercond. Sci. Technol. **5**, 205 (1992).

[52] P. Karen, H. Fjellvag, O. Braaten, A. Kjekshus, and H. Bratsberg, Acta Chem. Scand. **44**, 994 (1990).

[53] Z. P. Han, R. Dupree, D. McK. Paul, A. P. Howes, and L. W. J. Caves, Physica **181**, 355 (1991).

[54] C.-k. Chen. A. T. Boothroyd, Y.-l. Hu, F. R. Wondre, B. M. Wanklyn, and J. W. Hodby, Physica C **214**, 231 (1993).

[55] The ionic radius of Cm^{+3} is intermediate between those of Pr^{+3} and Nd^{+3}, L. Soderholm (private communication).

[56] T. Wada, N. Suzuki, A. Maeda, Y. Yabe, K. Uchinokura, S. Uchida, and S. Tanaka, Phys. Rev. B **39**, 9126 (1989); see also reports of the superconductivity of LaBaCaCu$_3$O$_7$: D. M. de

Leeuw, C. A. H. A. Mutsaers, H. A. M. van Hal, H. Verweij, A. H. Carim, and H. C. A. Smoorenburg, Physica C **156**, 126 (1988).

[57] D. P. Norton, D. H. Lowndes, B. C. Sales, J. D. Budai, B. C. Chakoumakos, and H. R. Kerchner, Phys. Rev. Lett. **66**, 1537 (1991).

[58] R.-k. Li, Z.-y. Chen, and Y.-t. Qian, Physica C **172**, 335 (1990).

[59] W. E. Pickett, Rev. Mod. Phys. **61**, 433 (1989) reviews the theory, including his own major contributions, and discusses how the Coulomb interactions convert a half-filled band into an insulator for materials in question. See also J. F. Annet, R. M. Martin, A. K. McMahan, and S. Satpathy, Phys. Rev. B **40**, 2620 (1989).

[60] O. Cohen, F. H. Potter, C. S. Rastomjee, and R. G. Egdell, Physica C **201**, 58 (1992).

[61] For a review, see D. Khomski, J. Supercond. **6**, 69 (1993).

[62] N. E. Phillips, R. A. Fisher, D. A. Wright, H. B. Radousky, J. L. Peng, L. Zhang, T. Goodwin, and R. L. Shelton, Bull. Am. Phys. Soc. **39**, 66 (1994).

[63] U. Neukirch, C. T. Simmons, P. Sladeczec, C. Laubschat, O. Strebel, G. Kaindl, and D. D. Sarma, Europhys. Lett. **5**, 567 (1988).

[64] J. S. Kang, J. W. Allen, Z. X. Shen, W. P. Ellis, J. J. Yeh, B. W. Lee, M. B. Maple, W. E. Spicer, and I. Lindau, J. Less-Commun Met. **148**, 121 (1989).

[65] L. Soderholm and G. L. Goodman, J. Solid State Chem. **81**, 121 (1989).

[66] L. Soderholm, C.-K. Loong, G. L. Goodman, and B. D. Dabroski, Phys. Rev. B **43**, 7921 (1991).

[67] J. Fink, N. Nücker, H. Romberg, M. Alexander, M. B. Maple, J. J. Neumeier, and J. W. Allen, Phys. Rev. B **42**, 4823 (1990).

[68] V. Nekvasil, E. Holland-Mortiz, and H.-D. Jostarndt, J. Magn. Magn. Mater. **117**, 11 (1992).

[69] H.-D. Jostarndt, W. J. Harnischmacher, and J. Kalenborn, Phys. Rev. B **46**, 14 872 (1992).

[70] F. W. Lytle, G. van der Laan, R. B. Gregor, E. M. Larson, C. E. Violet, and J. Wong, Phys. Rev. B **41**, 8955 (1990).

[71] A. Matsuda, K. Kinoshita, T. Ishii, H. Shibata, T. Watanabe, and T. Yamada, Phys. Rev. B **38**, 2910 (1988).

[72] C. H. Pennington and C. P. Slichter, in *Physical Properties of High-Temperature Superconductors,* edited by D. M. Ginsberg (World Scientific, Singapore), Vol. II, p. 269 *et seq.* (1990), and references therein.

[73] H. Ledbetter and M. Lei, Physica C **166**, 483 (1990).

[74] N. Koshida and K. Saito, Jpn. J. Appl. Phys. **29**, L1635 (1990); G. Rietveld, N.Y. Chen, and D. van der Marel, Phys. Rev. Lett. **69**, 2578 (1992).

[75] I. D. Brown and D. Altermatt, Acta Crystallogr. B **41**, 244 (1985); D. Altermatt and I. D. Brown, *ibid.* **41**, 241 (1985); I. D. Brown, J. Solid State Chem. **82**, 122 (1989); I. D. Brown and K. K. Wu, Acta Crystallogr. B **32**, 1957 (1976); I. D. Brown, *Structure and Bonding in Crystals,* edited by M. O'Keefe and A. Navrotsky (Academic, New York, 1980), Vol. II, p. 1.

[76] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939).