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Structural and magnetic properties of $MSr_2Y_{1.5}Ce_{0.5}Cu_2O_z$ (M-1222) compounds with M=Fe and Co

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The $MSr_2Y_{1.5}Ce_{0.5}Cu_2O_z$ (M-1222) compounds, with M=Fe and Co, have been synthesized through a solid-state reaction route. Both compounds crystallize in a tetragonal structure (space group $14/mmm$). A Rietveld structural refinement of the room-temperature neutron diffraction data for Fe-1222 reveals that nearly half the Fe remains at the M site, while the other half goes to the Cu site in the CuO_2 planes. Existence of Fe at two different lattice sites is also confirmed by ^{57}Fe Mössbauer spectroscopy from which it is inferred that ~50% of the total Fe occupies the Cu site in the CuO_2 planes as Fe^{3+}, whereas the other ~50% is located at the M site with ~40% as Fe^{4+} and ~10% as Fe^{3+}. For the M≡Co compound, nearly 84% of Co remains at its designated M site, while the rest occupies the Cu site in the CuO_2 planes. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1688256]

The $MSr_2Y_{1.5}Ce_{0.5}Cu_2O_z$ (M-1222, M=Fe and Co) compounds are derived from $CuBa_2YCu_2O_{7-\delta}$ (Cu-1212) by replacing the charge-reservoir Cu(1) with M, and inserting a three-layer fluorite-type block (Y,Ce)–O_2–(Y,Ce), instead of the single oxygen-free Y layer between the two CuO_2 planes of Cu-1212 structure.[1] Some of us recently reported the phase formation of various $MSr_2YCu_2O_z$ (M-1212) compounds with M=Fe[2] and Co.[3] In the M-1212 compounds, though M cations are expected to reside at the Cu(1) site in the charge reservoir layer with full occupancy, it was found that, to some extent, they occupy the Cu(2) plane site also.[2,3] Particularly, in air annealed Fe-1212 compound, Fe cations were distributed equally at both Cu(1) and Cu(2) sites. In the case of Co-1212, the Co cations occupancy was complete at the Cu(1) site alone. These results were confirmed by neutron powder diffraction and ^{57}Fe Mössbauer spectroscopy studies.[2,3] Further, interesting structural changes, pertaining to space group and unit cell doubling, were observed for Co-1212.[3,4]

Samples of $MSr_2(Y_{3/4}Ce_{1/4})_2Cu_2O_z$ (M=Fe, Co) were synthesized by the solid-state reaction method. ^{57}Fe Mössbauer spectrum was recorded at room temperature in trans-

mission geometry for the Fe-1222 sample. Magnetization measurements as a function of temperature (4.2–300 K) were carried out using a SQUID magnetometer (Quantum Design: MPMS-XL).

Room temperature neutron powder diffraction (NPD) patterns for the M-1222 (M=Fe and Co) samples were found to be nearly free of any impurities (see Fig. 1). The NPD data were analyzed by the Rietveld refinement procedure using the generalized structural analysis system program. Structural parameters, such as atomic coordinates, occupancies, and thermal parameters (U_{iso}) for different atoms including variously named oxygen atoms are listed in Table I. The diffraction patterns were readily fitted in a tetragonal structure (space group $I4/mmm$) lattice parameters are $a=3.82288(78)$ Å and $c=28.1203(57)$ Å for Fe compound and $a=3.83158(34)$ Å and $c=28.1659(24)$ Å for Co compound The M-1222 compounds are structurally related to the $CuBa_2YCu_2O_{7-\delta}$ (Cu-1212) compounds with Cu(1) in the charge reservoir replaced by M. Further, a three-layer fluorite-type block $(Y_{3/4}Ce_{1/4})–O_2–(Y_{3/4}Ce_{1/4})$ is inserted between the two CuO_2 planes in M-1212 compounds instead of the rare earth Y layer in Cu-1212.[1] The M-1222 structure may be viewed as a layer sequence of $–MO_{1\pm\delta}–SrO–CuO_2–(Y,Ce)–O_2–(Y,Ce)–CuO_2–SrO–MO_{1\pm\delta}$. We should mention here that, as shown later in this section, the M cation may go to both the chain Cu(1) site

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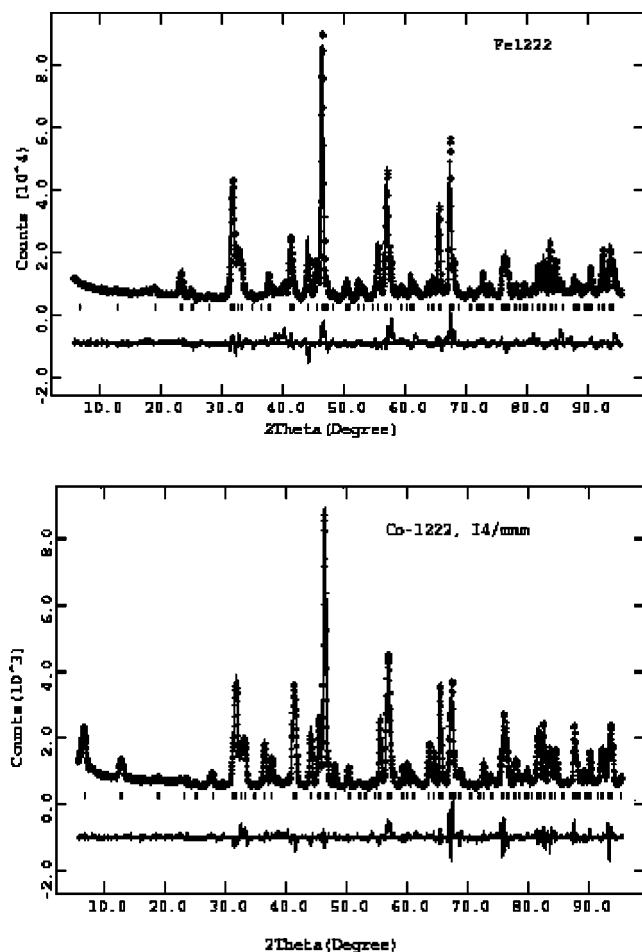[b]Presenting author.

FIG. 1. Observed and fitted neutron diffraction patterns for $MSr_2(Y_{3/4}Ce_{1/4})_2Cu_2O_z$ (M=Fe,Co).

TABLE I. Refined structural parameters for $MSr_2Y_{1.5}Ce_{0.5}Cu_2O_z$ compounds (M=Fe and Co), including atomic coordinates, occupancies, and thermal parameters (U_{iso}). Space group is $I4/mmm$, and lattice parameters are $a=3.82288(78)$ Å and $c=28.1203(57)$ Å for Fe compound and $a=3.83158(34)$ Å and $c=28.1659(24)$ Å for Co compound. Statistical errors are given in brackets, which are usually 2–3 times smaller than true values in Rietveld analysis.

Atom	Fe-1222 $R_{wp}=10.00\%$	Co-1222 $R_{wp}=8.66\%$
M@Cu(1) at $2a$ (x,y,z)	0, 0, 0	0, 0, 0
Occupancy	0.60(4)	0.83(3)
$U_{iso}(nm^2)$	2.2(2)	7.4(9)
M@Cu(2) at $4e$ (x,y,z)	0, 0, 0.14100(20)	0, 0, 0.14381(16)
Occupancy	0.20(2)	0.09(1)
$U_{iso}(nm^2)$	0.8(1)	0.6(1)
Sr at $4e$ (x,y,z)	0, 0, 0.42466(28)	0, 0, 0.41903(15)
Occupancy	1	1
$U_{iso}(nm^2)$	3.0(2)	1.1(1)
Y at $4e$ (x,y,z)	0, 0, 0.29724(22)	0, 0, 0.29451(16)
Occupancy	0.75	0.75
$U_{iso}(nm^2)$	1.5(2)	1.0(1)
Ce at $4e$ (x,y,z)	0, 0, 0.29724(22)	0, 0, 0.29451(16)
Occupancy	0.25	0.25
$U_{iso}(nm^2)$	1.5(2)	1.0(1)
Cu(2) at $4e$ (x,y,z)	0, 0, 0.14100(20)	0, 0, 0.14381(16)
Occupancy	0.80(2)	0.91(2)
$U_{iso}(nm^2)$	0.8(1)	0.6(1)
O(1) at $4c$ (x,y,z)	0.090(5), $\frac{1}{2}$, 0	0.2744(35), $\frac{1}{2}$, 0
Occupancy	0.32(1)	0.27(1)
$U_{iso}(nm^2)$	4.4(9)	2.1(5)
O(2) at $8g$ (x,y,z)	0, $\frac{1}{2}$, 0.15060(18)	0, $\frac{1}{2}$, 0.15011(14)
Occupancy	1	1
$U_{iso}(A^{02})$	2.7(2)	1.7(1)
O(4) at $4e$ (x,y,z)	0, 0, 0.06781(36)	0, 0, 0.0605(20)
Occupancy	1	1
$U_{iso}(nm^2)$	4.4(3)	2.9(2)
O(6) at $4d$ (x,y,z)	0, $\frac{1}{2}$, $\frac{1}{4}$	0, $\frac{1}{2}$, $\frac{1}{4}$
Occupancy	1	1
$U_{iso}(nm^2)$	1.9(2)	1.5(2)
Cu(1) at $2a$ (x,y,z)	0, 0, 0	0, 0, 0
Occupancy	0.40(4)	0.17(3)
$U_{iso}(nm^2)$	2.2(2)	7.4(9)

and the plane Cu(2) site, and the related layers may have variable composition. The oxygen sites in the CuO_2 plane are named as O(2) and O(3), while that in the SrO plane is called O(4). The oxygen sites in the $CuO_{1\pm\delta}$ layer are named O(1) (along the *b* axis) and O(5) (along the *a* axis). The oxygen site in the $(Y,Ce)_2O_2$–fluorite-type block is named O(6). In tetragonal structures, with lattice parameters $a=b$, the O(1), O(5) and O(2), O(3) become indistinguishable and hence their occupancies remain the same. Also, the oxygen varies only in $CuO_{1\pm\delta}$ chains of 1212 or 1222 structures, hence except for O(1)/O(5) other oxygen sites are kept as fully occupied. The overall oxygen content for Fe-1222 and Co-1222 determined from various oxygen occupancies is, respectively, 9.28(3) and 9.08(2) (Table I).

It is interesting to point out that in contrast to the structure of Cu-based 1212 compound (space group $P4/mmm$), the structure of Co-based 1212 compound changes to the $Ima2$ space group.[3] In the Co-based 1212 structure, the Co sites in the alternate charge reservoir layers are found shifted with respect to each other, leading to a doubling of the unit cell, which is responsible for the change in its space group.[3,4] However, as shown by the NPD data (see Fig. 1), the space group $I4/mmm$, found for both Fe-1222 and Co-1222 systems, is the same as that for the Cu-1222 system. For Fe/Co-1222, unlike Co-1212, with an inserted flourite-type block, the unit cell is body centered and further doubling of the unit

cell is not required. However, an important difference between Fe-1222 and Co-1222 follows from the arrangement of oxygen around the chain site M cation. For example the O(1) site *x* coordinate for Co-1222 and Fe-1222 are, respectively, 0.274(4) Å and 0.090(5) Å. The shift in the position of O(1) for presently studied Co-1222 has also been revealed for Co-1212.[3] In fact the Fe-1222 has the usual Cu-1222 like square-planar geometry of MO sheet, whereas the latter shows tetrahedrons of MO_4. This result can be further understood, as shown below, by the relative occupancies of Fe and Co at Cu(1) and Cu(2) sites.

The refinement of NPD data for Fe-1222 (Table I) shows that nearly half (~60%) of Fe occupies the expected Cu(1) site in chains, and the remaining goes to the Cu(2) site in the CuO_2 planes. Existence of Fe at two different lattice sites, in the presently studied Fe-1222 sample, is also confirmed by [57]Fe Mössbauer spectroscopy, which revealed three distinct
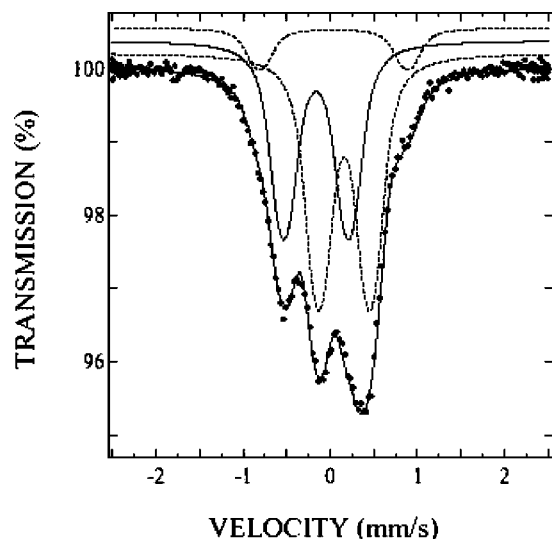
FIG. 2. Fitting of the ^{57}Fe Mössbauer spectrum recorded at room temperature for the Fe-1222 sample. The components used into fitting are displayed above the data. Reading from topmost they are Fe^{3+} at $Cu(1)$, Fe^{4+} at $Cu(1)$, and Fe^{3+} at $Cu(2)$.

FIG. 3. Magnetization vs temperature plots for Fe-1222, the inset shows M vs H behavior at 5, 50, and 100 K.

components (Fig. 2). These clearly arise from Fe occupying various lattice sites, or the same lattice sites with different oxygen coordination. Considering that the neutron diffraction data indicate that a substantial amount of Fe is found on both $Cu(1)$ and $Cu(2)$ sites, it is necessary to assume that the two major Fe components originate from different lattice sites. The most intense component (which covers 51% of the total area) has an isomer shift of 0.26 mm/s and is clearly Fe^{3+}. The next (covering 40% of the total area) has a negative isomer shift of -0.05 mm/s, and is readily assigned to Fe^{4+}. The average (formula) valence of Fe is $+3.5$ (assuming z to be 9, while Ce is assumed to be in a $4+$ state), i.e., charge neutrality is almost fulfilled with this assignment. The formation of Fe^{2+} is not considered here due to the oxidative synthesis conditions. Besides, the isomer shift of Fe^{2+} is always very large. The weakest component covered 9% of the total intensity. It had an isomer shift of 0.13 mm/s, i.e., quite compatible with Fe^{3+}. Assigning the two Fe^{3+} components to the $Cu(2)$ site and the Fe^{4+} component to the $Cu(1)$ site would yield the best agreement with the neutron results. However, this is not the conclusion we arrived at. In fact Fe^{4+} and the weak Fe^{3+} component are believed to occupy the $Cu(1)$ site, where the larger oxygen variations of the $CuO_{1\pm\delta}$ chains supposedly more easily incorporate Fe with various coordinations and high valences.[5] This would lead to a 50% versus 50% ratio of Fe at $Cu(1)$ and $Cu(2)$ sites, respectively. In contrast, in the case of Co-1222, the NPD refinement (Table I) shows nearly 84% of Co at its designated $Cu(1)$ site and the rest at the $Cu(2)$ plane sites. When compared with M-1212 type compounds, an identical situation is seen for Fe-1212 and Co-1212,[2] where Fe is intermixed at both $Cu(1)$ and $Cu(2)$ sites[2] and Co resides with full occupancy at the $Cu(1)$ site.[3]

It may be interesting to remark that avoidance of intermixing of Fe at $Cu(1)$ and $Cu(2)$ sites results in supercon-
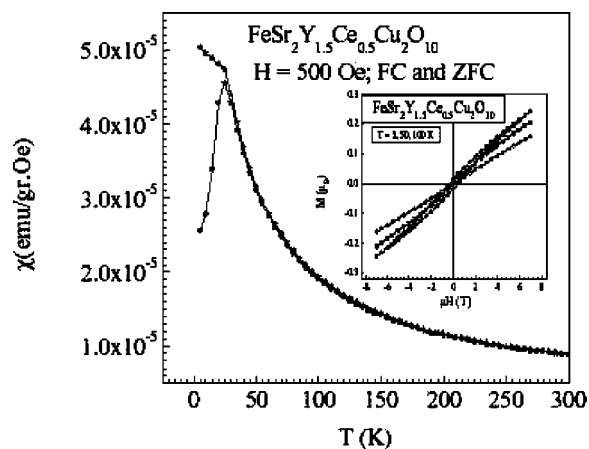
ductivity in Fe-1212,[6] although the same is not clear in the case of Co-1212. Thus, neither of the Fe-1222 and Co-1222 compounds were expected to show superconductivity. Figure 3 shows the dc susceptibility versus temperature (χ-T) behavior for the Fe-1222 sample in an applied field of 500 Oe. A cusp in the susceptibility appears in the zero-field-cooled (ZFC) curve at $T\sim25$ K, where the field-cooled (FC) curve also shows a break and a large decrease in slope. Further, in the same figure, a clear branching of ZFC and FC curves at the same temperature is also observed. At this stage, it is interesting to note the behavior of isothermal magnetization (M) versus field (H) measured at different temperatures, e.g., $T=5$, 50, and 100 K, shown in the inset of Fig. 3. At 100 K, the $M-H$ curve is nearly linear and the sample is in a nearly pure paramagnetic state. However, at $T\leqslant50$ K, the $M-H$ curves show a strong nonlinearity along with the appearance of hysteresis in $M-H$ data at 5 K. In the case of Co-1222, the overall behavior is not very different from that observed in the case of Fe-1222. The break in the slope of FC $M(T)$ occurs at around 80 K, however, the slope increases at lower temperatures. The cusp in ZFC $M(T)$ and the branching occur at around 40 K. Thus a magnetic scenario similar to that of Fe-1222 seems to be present. The compounds (Fe-1222 and Co-1222) contain a mixture of Fe and Co in different valence states and, therefore, of Fe and Co ions with different magnetic moments. In this case, any antiferromagnetic interaction may lead to a ferrimagnetic behavior because of noncompensating moments. The differences in the characteristic temperatures observed for the Fe-1222 and Co-1222 systems may be due to the different amount of intermixing of Fe/Co at $Cu(I)$ and $Cu(II)$ sites. Finally, we would like to remark that the underlying magnetic ordering in Fe/Co-1222 is not so straightforward. For a clearer picture, neutron diffraction studies on these compounds in the magnetically ordered state are desirable.

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