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Substitution effect on ferromagnetism in $La_4Ba_2Cu_2O_{10}$

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The magnetic properties of $(La_{1-x}R_x)_4Ba_2Cu_2O_{10}$ were studied for $R=$Nd, Sm, Gd, and Eu, of which the end material, $La_4Ba_2Cu_2O_{10}$, is known as a rather exceptional ferromagnet among the known copper-oxide insulators. It was found that the average ionic radius of the elements at the La site r determines the solubility limit of R elements. When r is larger than ~ 1.11 Å, the compound has the $La_4Ba_2Cu_2O_{10}$-type structure, while for smaller r, the Y_2BaCuO_5 type structure is formed. The magnetic behavior of the compounds depended on the R element; even a rather small amount of Nd altered the ferromagnetic ground state to an antiferromagnetic one, with a possible spin-glass state in between. For $R=$Sm and Gd, the experimental results suggest a similar change of ferromagnetism to antiferromagnetism, but a ferrimagnetlike behavior was observed for intermediate compositions. On the other hand, ferromagnetism resided up to the solubility limit for $R=$Eu. The application of high pressure up to 8.0 GPa hardly affected the magnetism of $La_4Ba_2Cu_2O_{10}$. This result, as well as the results of Rietveld analyses of R-substituted $La_4Ba_2Cu_2O_{10}$, indicate that the reduction of ferromagnetism with the increase in x is not attributable to the structural change induced by the substitution, the chemical pressure effect.

I. INTRODUCTION

Copper oxides with the general formulas R_2BaCuO_5 have two different structural types, depending on R which denotes Y or one of the rare-earth elements.[1,2] The first type of structure has an orthorhombic symmetry with space group $Pnma$, and this phase, the so-called green phase, is well known as the impurity phase of high-temperature superconductors. The other phase is often called the brown phase, and exhibits a tetragonal symmetry with space group $P4/mbm$. To distinguish these two phases, we call the former the 211 phase throughout this paper, while the latter, the 422 phase.

In 1990, Mizuno *et al.* found that La422 undergoes a ferromagnetic (FM) transition at 5.2 K.[3] This is rather unusual among the copper oxides, because most of the known insulating cuprates have antiferromagnetic (AFM) ground states, and therefore, the ferromagnetism in La422 drew some theoretical interests.[4,5] Tasaki has pointed out that the magnetic paths formed by Cu^{2+}, La^{3+} and O^{2-} ions along the c-axis direction may be mapped under some assumptions on a model lattice that falls into the class of nearly flat-band ferromagnetism.[4] It has been argued that the Hubbard model with a flat-band may possess a FM ground state.[4,6–9] In this connection, it is interesting to note that the band calculation according to a spin-polarized local-density approximation revealed a very small dispersion for the bands at the Fermi energy.[10] Feldkemper *et al.*, on the other hand, showed that interference between inequivalent superexchange paths can alter the magnetic interaction between two magnetic sites.[5] They have argued that the AFM coupling along the (001) direction in La422 is substantially reduced due to the interference effect, and claimed that this leads to a net FM interaction.[5]

$Nd_4Ba_2Cu_2O_{10}$ (Nd422) is isostructural to La422, but is known to exhibit an AFM ordering at low temperatures.[11,12] For $Pr_4Ba_2Cu_2O_{10}$ (Pr422), a weak FM behavior was found at low temperatures, but this was attributed to canted moments of Pr and Cu, and the overall order is AFM.[13] Hence, substituting a different rare-earth element for La can greatly affect the ferromagnetism in La422. Salinas-Sánchez and Sáez-Puche substituted half of the La site of La422 with Nd or Eu, and concluded that the presence of Nd^{3+} in-between the superexchange path of Cu ions destroy the FM order, while nonmagnetic Eu^{3+} ions have no effect on the magnetic interaction.[14]

In this study, we have substituted La with various rare-earth elements and changed systematically the ratio of La to R to examine the influence of magnetic moments on the La site to the magnetic behavior. Samples of $(La_{1-x}R_x)_4Ba_2Cu_2O_{10}$ [(La,R)422] with $R=$Nd, Sm, Gd, and Eu were prepared, and the change in structure and magnetic behavior upon substitution was investigated. Further, because of the possibility that structural distortion induced by foreign atoms, the so-called chemical pressure effect, may play a role in the observed change of magnetism, we also studied La422 under high pressure up to 8.0 GPa. The substitution of La by a rare-earth ion with magnetic moments affected seriously the FM state of La422, and various magnetic behaviors were observed. On the other hand, the application of high pressure had only weak effect on the FM interaction, at least within our experimentally accessible range.

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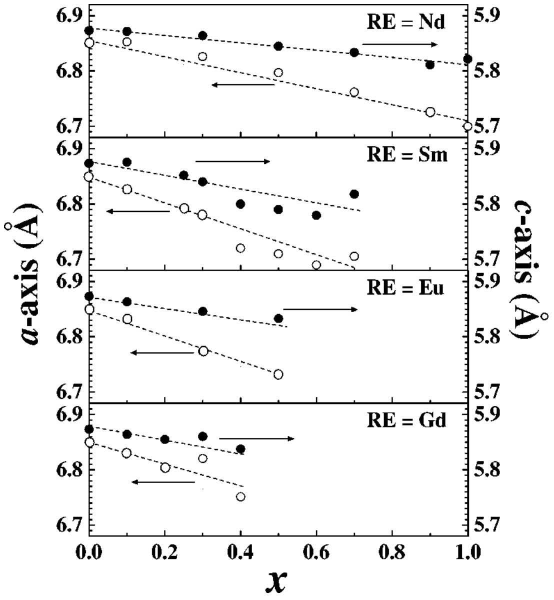

FIG. 1. Lattice constants of (La,R)422 samples (R $=$Nd, Sm, Gd, Eu). While $R=$Nd samples are single phased for the whole composition range, a solubility limit exists between x $=0.5$ and 0.6 for $R=$Sm and Eu, and between $x=0.4$ and 0.5 for $R=$Gd. The dashed lines are guides to eye.

II. EXPERIMENT

(La,R)422 with $R=$Nd, Sm, Gd, and Eu were prepared by sintering stoichiometric amounts of R_2O_3 (R $=$La, Nd, Sm, Gd, Eu) and $BaCuO_2$ at 900 °C for 12 h in air. The reactant was reground and sintered twice in air at 1000 °C for 12 h. The purity of the samples was checked by powder x-ray-diffraction measurements. Lattice constants were calculated from the position of some of the high angle peaks using a least-squares fitting procedure. We have also analyzed the detailed structure of some of the samples, using the Rietveld method. The diffraction data for the Rietveld analyses were accumulated by Rigaku RINT-2000 using graphite monochromatized Cu K_α radiation in the 2θ range of 10–150°. The scanning step was 0.02°, and the counting time per step was 60 s. The refinement of the structure was performed using the Rietveld refinement program, RIETAN.[15]

The magnetic susceptibility of the samples was measured using a superconducting quantum interference device magnetometer in the temperature range of 2.0–300 K. The effect of high pressure on La422 was investigated by measuring the lattice constants and ac-magnetic susceptibility. Powder x-ray diffraction under isotropical high pressure was carried out up to 6.0 GPa using a diamond-anvil cell and an imaging plate. An organic solvent was used as a pressure transmitting medium, and the pressure was checked by monitoring the wavelength of the R_1 fluorescence of small specimens of ruby. On the other hand, a cubic-anvil cell was used for the ac-magnetization measurements filled with a mixture of Fluorinert FC70 and FC77 as a pressure transmitting medium. The temperature was varied in the range of 2.0–300 K and the pressures up to 8.0 GPa.

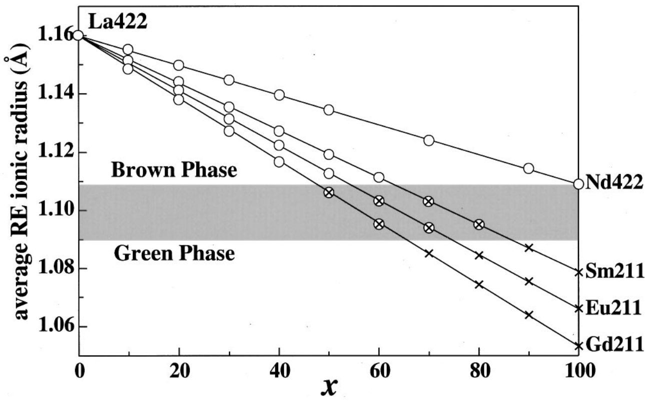

FIG. 2. The relation between the average La(R)-site ionic-radii (r) and crystal structure of nominal (La,R)422 (R $=$Nd Sm, Gd, and Eu) samples. For $R=$Nd, the brown phase type structure is formed over the whole range of $x(0\leqslant x\leqslant 1)$. For R $=$Sm, Gd, and Eu, the samples are single phased only when r is sufficiently large. When r is smaller than ~1.11 Å, the samples involve the 211 phase, the green phase.

III. RESULTS

Figure 1 shows the x dependence of the lattice constants of the single-phased samples of (La,R)422 (R $=$Nd, Sm, Gd, Eu) prepared in this study. For $R=$Nd, the x-ray diffraction experiments confirmed that the samples are single-phased over the whole concentration range ($0\leqslant x$ $\leqslant 1$). On the other hand, when La is substituted by R $=$Sm, Eu, or Gd, the $x=1$ samples form the 211 phase, the so-called green phase, and there exists a solubility limit for the 422 phase. We found that for $R=$Eu, for instance, the samples in the concentration range of $0\leqslant x\leqslant 0.5$ are single-phased and have the 422 structure, the brown phase structure. Samples with $x=0.6$ or 0.7 are mixtures of the brown and green phases, and for $x\geqslant 0.8$, no reflection peak due to the brown phase was detected in the x-ray diffraction pattern within the experimental sensitivity. As expected, the lattice constants of the 422 phase obey Vegard's rule and decrease linearly with x up to the solubility limit.

Figure 2 shows the relation between the crystal structure observed in the diffraction experiment and the average ionic radius of the elements at the La site. Here, we have used the ionic radii of the R elements tabulated in the literature.[16] It can be seen that the average size of R apparently determines the phase of the sample; If the average radius is larger than 1.11 Å, the 422 structure is formed, while when smaller than 1.09 Å, the material has the 211 structure.

Figure 3(a) shows the temperature dependence of magnetization of (La,Nd)422 samples up to $x=0.3$ at low temperature. The external field for these measurements was 10 Oe. The result of the $x=0$ sample is in a good agreement with the report by Mizuno *et al.*;[3] Magnetization increased divergently below 5.2 K, and a hysteresis was observed in the isothermal magnetization loop as shown in the inset, indicating the formation of a FM ground state. Magnetization at 5.5 T, 2.0 K is about 0.91 μ_B/f.u., which suggests that almost all Cu^{2+} spins participate in the magnetic order. The temperature dependence of the magnetic susceptibility of La422 at higher temperature followed well the Curie-Weiss behavior between 50 and 300 K. A fit that accounts both for the

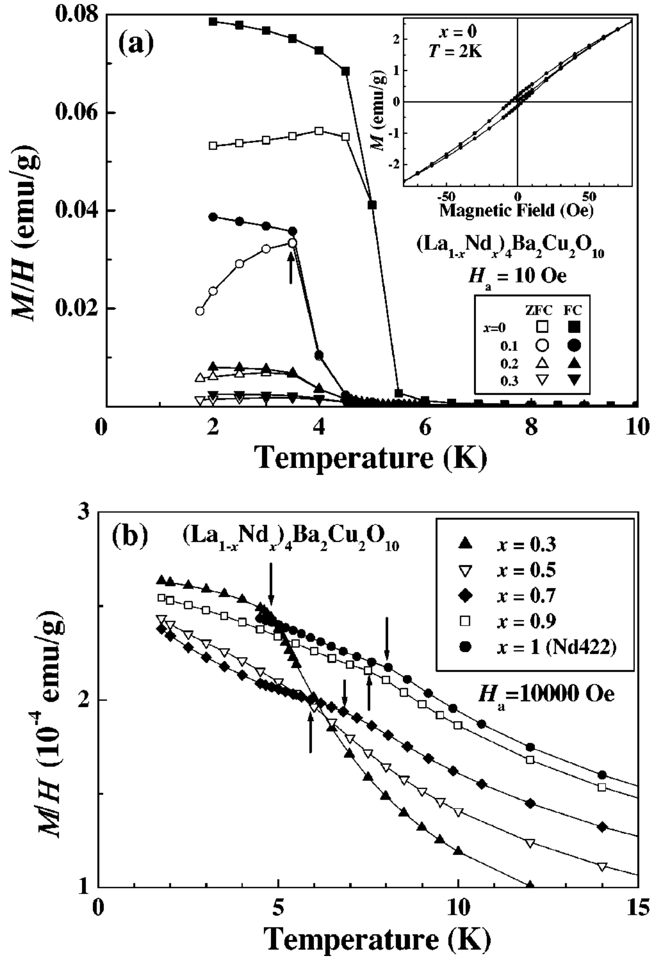

FIG. 3. The temperature dependence of magnetic susceptibility of $(La_{1-x}Nd_x)_4Ba_2Cu_2O_{10}$ samples, (a) $0 \leqslant x \leqslant 0.3$ measured at 10 Oe, and (b) $0.3 \leqslant x \leqslant 1.0$ measured at 10 000 Oe. The inset to (a) shows the isothermal magnetization loop measured on the $x=0$ sample at 2 K. The arrows in (b) indicate the cusplike structure, attributable to an AFM transition.

Curie-Weiss behavior and a temperature independent term of susceptibility revealed $1.72\mu_B$ per Cu^{2+} ion for the effective magnetic moment (p_{eff}), which is again in a good agreement with the value reported by Mizuno *et al.*, $p_{\mathrm{eff}} = 1.66\mu_B$.[3] The value of p_{eff} is close to the magnetic moment of Cu^{2+} with quenched orbitals, $p_{\mathrm{eff}} = 1.73\mu_B$, indicating that the magnetic moments of La422 come from Cu^{2+} ions.

As can be seen from Fig. 3(a), the magnetization at 2 K rapidly decreases with substituting La by Nd up to $x=0.3$. In Fig. 3(b) is shown the temperature dependence of susceptibility of samples with $x \geqslant 0.3$ with an expanded scale. The applied field for these measurements was 10 000 Oe. The temperature dependence of susceptibility shown in Fig. 3(b), is far from a FM behavior and exhibits a cusplike structure as indicated by the arrows, which can be ascribed to an AFM transition. Hence, these results indicate that the magnetism of La422 changes from a FM to an AFM state at around $x=0.3$ when Nd substitutes La.

We shall also comment on the splitting of the zero-field-cooling (ZFC) and field-cooling (FC) magnetization data of some of the Nd-substituted samples as shown in Fig. 3(a). In fact, such a thermal history effect is also obvious for the nonsubstituted sample ($x=0$), but the ZFC magnetization of the pure sample below the Curie point (T_C) behaved differently from that of moderately Nd-substituted samples. For the latter samples, the ZFC magnetization curve exhibited a cusp below T_C, and showed a tendency of approaching zero at $T=0$. This behavior suggests the possibility of a spin-glass formation with a phase transition temperature lower than T_C. Although, the dc magnetization alone is not conclusive evidence for the spin glass, it would be worth pointing out that the published data of some pyrochlore oxides, which were concluded to be reentrant spin glasses,[17,18] are very similar to the magnetization data of moderately ($0.1 \leqslant x \leqslant 0.3$) Nd-substituted samples shown here. For the $x=0$ sample, on the other hand, magnetization below T_C is only weakly dependent on temperature for both ZFC and FC measurements and differs from the expected behavior for a spin glass. Hence, the temperature hysteresis of the $x=0$ sample can be well understood by the spontaneous magnetization of the FM state.

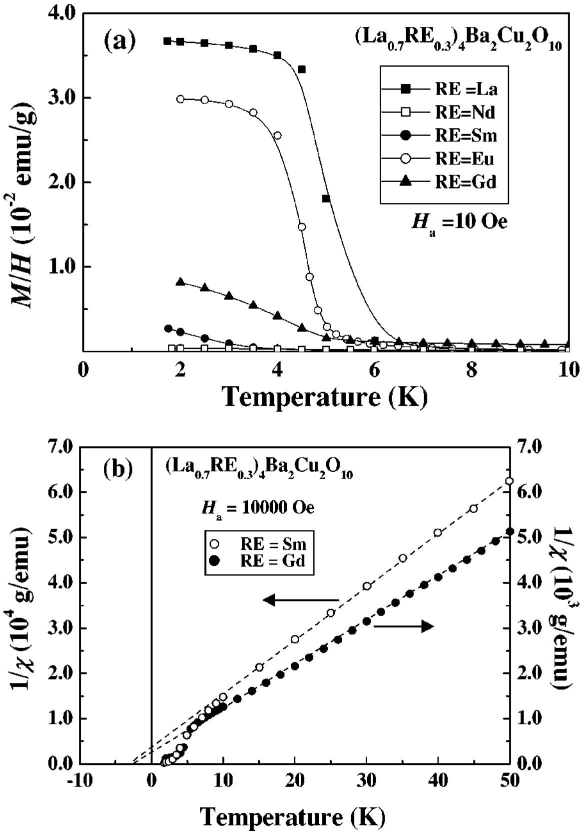

FIG. 4. (a) The temperature dependence of magnetic susceptibility of $(La_{0.7}R_{0.3})_4Ba_2Cu_2O_{10}$ (R=La, Nd, Sm, Gd, Eu). The applied field is 10 Oe. (b) The temperature dependence of inverse susceptibility of the $x=0.3$ substituted R=Sm and Gd samples measured at 10 000 Oe. The dashed lines are fit to the Curie-Weiss behavior at high temperature. Extrapolation of the high-temperature data intercepts the temperature axis with a negative value.

Figure 4 displays the temperature dependence of magnetization measured at 10 Oe for all $x=0.3$ samples with various R elements measured by the FC mode. For R=Eu, the FM transition is quite obvious. On the other hand, substitution of Sm or Gd for La made the transition rather dull, and the susceptibility at 2 K decreased substantially. This suggests the weakening of the FM interaction. However, the

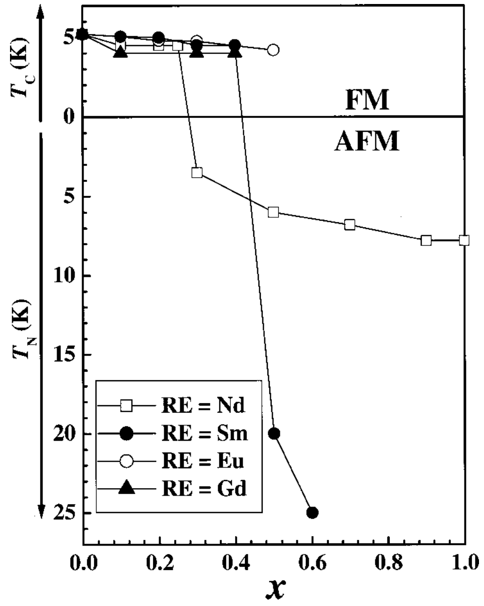

FIG. 5. A plot of Curie and Néel temperatures of $(La_{1-x}R_x)_4Ba_2Cu_2O_{10}$ ($R=$Nd, Sm, Eu, Gd) samples as a function of x. While substitution of Nd, Sm or Gd affects seriously the FM state of La422, the Eu substitution has a much less influence.

isothermal magnetization loops of the $R=$Sm and Gd samples still exhibited small hysteresis.

In contrast to the spin-glass-like behavior in Nd-substituted samples, no tendency of approaching zero at $T=0$ was observed for the ZFC magnetization when $R=$Sm and Gd. Instead, we observed a ferrimagnetlike behavior for these samples. Figure 4(b) shows the temperature dependence of the inverse susceptibility (ZFC) of the $x=0.3$ samples of $R=$Sm and Gd measured at 10 000 Oe. The high-temperature region follows well the Curie-Weiss behavior. However, the inverse susceptibility is a convex curve near the transition temperature, and the extrapolation of the high-temperature region intercepts the temperature axis at a negative value, which is an expected behavior for a ferrimagnet. Hence, the frustration introduced by the substitution of Sm or Gd for La seems to lead to a ferrimagnet ground state rather than a spin-glass order.

IV. DISCUSSION

Figure 5 is a plot of Curie and Néel temperatures determined from the magnetization measurements as a function of the amount of substitution, x. Curie temperature was determined as the temperature above which no hysteresis was observed in the magnetization loop, while Néel temperature was determined by the position of the cusplike structure in the susceptibility data, similar to those indicated by the arrows in Fig. 3(b). As mentioned above, we have also observed a spin-glass-like behavior below T_C for moderately Nd-substituted samples. This is quite conceivable, since (La,Nd)422 may be considered as a random mixture of a ferromagnet and an antiferromagnet, with frustrated magnetic interactions. However, because our present data are not sufficient to unambiguously conclude whether the magnetic state is a spin glass or not, this possibility is not included in Fig. 5. Similarly, the possibilities of ferrimagnetism in the $R=$Sm and Gd systems are also not shown.

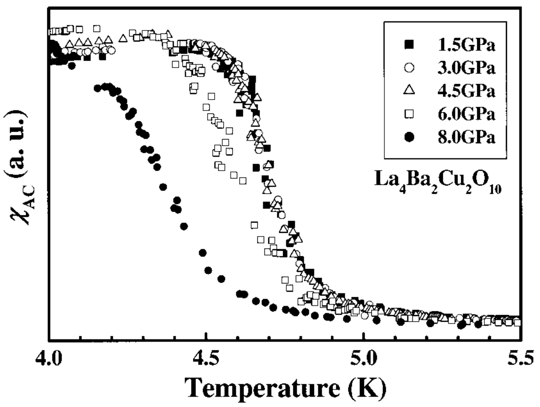

FIG. 6. The temperature dependence of the real part of ac susceptibility of La422 measured under high pressure up to 8.0 GPa. The signal is normalized to the value at 10 K.

The results plotted in Fig. 5 imply that the magnetic interaction between Cu changes from FM to AFM when Nd or Sm is substituted for La. Spontaneous magnetization was observed up to the solubility limit for $R=$Gd, but the saturation moment suffered a large reduction. On the other hand, the FM interaction is only weakly affected by Eu substitution. Both trivalent La and Eu have nonmagnetic ground states, and at sufficiently low temperature, where only the ground state is populated, no magnetic moment is present on the La(Eu) site of (La,Eu)422. Therefore, the results shown in Fig. 5 are consistent with the report by Salinas-Sánches and Sáez-Puche, who studied a $x=0.5$ Eu-substituted sample, and concluded that the magnetic ground state is a ferromagnet.[14]

Substitution of a foreign element usually introduces a structural stress into the crystal, the so-called chemical pressure effect. It is well known that the exchange interaction may alter when the bond lengths or bond angles between the magnetic moments are varied. Therefore, the observed change in magnetism with substitution may have been caused to some extent by the chemical pressure effect. To check this possibility, we have studied the magnetic behavior of La422 at high pressures. Figure 6 shows the real part of the ac susceptibility measured under pressure up to the 8.0 GPa. The signal is normalized to the value at 10 K. Obviously, the application of high pressure has only a small effect on the FM phase transition.

Figure 7 plots the Curie and Néel temperatures against the c-axis length for La422 under high pressure and for the single-phased R-substituted samples. The application of high pressure reduced the lattice constants of La422 linearly, and the c-axis length at about 3.0 GPa was almost the same as that of Nd422 at ambient pressure. Nevertheless, the Curie temperature of La422 was almost the same up to 6.0 GPa. A further increase of pressure to 8.0 GPa reduced T_C, but only by 0.4 K. Hence, the FM interaction in La422 is quite robust against high pressure, even the interion distance along the c-axis direction is shorter than that of AFM Nd422 when the pressure exceeds about 3.0 GPa. As a result, we conclude that the structural distortion due to substitution has only a weak, if any, effect on the FM interaction.

Figure 8 shows the relation between lattice constants a

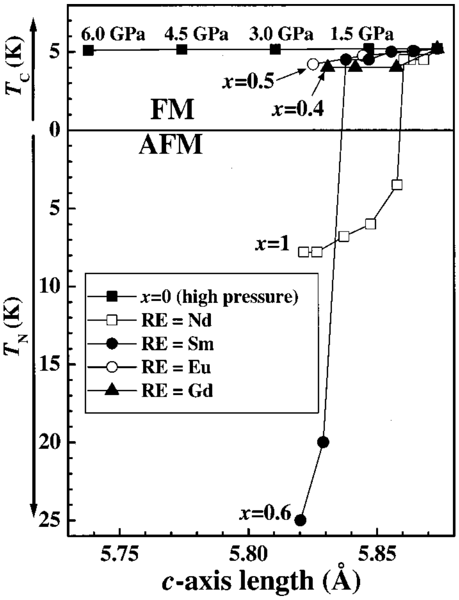

FIG. 7. The Curie and Néel temperatures of the (La,R)422 samples as a function of the c-axis length. The data of stoichiometric La422 under high pressure is also plotted. All the samples included in this figure are single-phased with the 422 structure, the tetragonal brown phase.

and c determined by the Rietveld analyses of the R-substituted samples. The relation between the lattice constants of La422 under high pressure, which was determined by the least-square fittings to the peak positions of the diffraction data, is also plotted in the figure. The dashed line in Fig. 8 indicates how the lattice constants should vary when the deformation of the sample is isotropic. Obviously, the application of high pressure leads to a stronger contraction along the c-axis direction, while R substitution contracts the sample faster along the a-axis direction. Very interestingly, the plot indicates that all data measured on R-substituted La422 falls on a single line irrespective of the magnetic state. On the other hand, the ratio between the lattice constants alters in a different way when La422 is subjected to high pressure. Ferromagnetism was observed in both Eu-substituted samples and pure La422 under high pressure. Therefore, the result shown in Fig. 8 is another support that structural changes have only weak, if any, effect to the magnetism of La422.

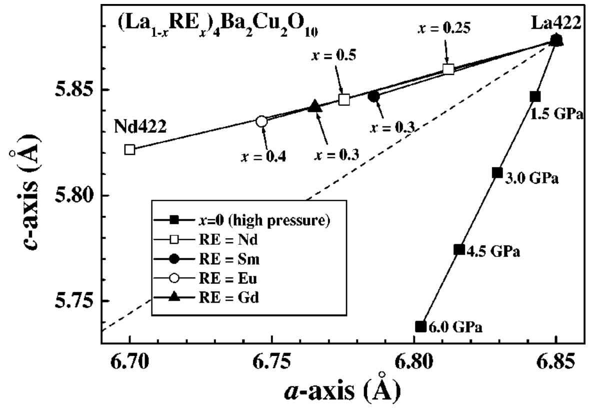

FIG. 8. The relation between lattice constants c and a. The data for $(La_{1-x}R_x)_4Ba_2Cu_2O_{10}$ (R = Nd, Sm, Gd, Eu) were determined from Rietveld analyses, while those for La422 under high pressure were determined from least-square fittings to the positions of reflection peaks in the powder x-ray diffraction data. The dashed line corresponds to a constant ratio of c to a.

V. CONCLUSIONS

In conclusion, we have studied the change of magnetic behaviors of La422 upon substituting La with Nd, Sm, Gd or Eu. We investigated also the high-pressure effect on the FM state of La422. While the substitution of Nd, Sm, or Gd for La drastically altered the magnetic state and a variety of magnetic behavior was observed, the substitution by Eu, which is nonmagnetic in the trivalent state, led to only a small change in the Curie temperature. Further, the application of a high pressure up to 8.0 GPa barely affected the FM order in La422. These results indicate that the nonexistence of a magnetic ion at the La site is crucially important for the FM state in La422, while the structural distortion has virtually no effect on the FM interaction, within the present experimentally accessed range.

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