PHYSICAL REVIEW B, VOLUME 65, 024441

Specific heat and thermal expansion of $La_{0.65}Ca_{0.35}MnO_3$: Magnetic-field dependence, isotope effect, and evidence for a first-order phase transition

J. E. Gordon,[1] C. Marcenat,[2] J. P. Franck,[3] I. Isaac,[3] Guanwen Zhang,[3] R. Lortz,[4,5] C. Meingast,[4] F. Bouquet,[6]
R. A. Fisher,[6] and N. E. Phillips[6]
[1]*Physics Department, Amherst College, Amherst, Massachusetts 01002*
[2]*DRFMC, SPSMS, CEA-Grenoble, 38054, Grenoble, France*
[3]*Department of Physics, University of Alberta, Edmonton, Alberta, Canada T6G2J1*
[4]*Forschungszentrum Karlsruhe, Institut für Festkörperphysik, 76021 Karlsruhe, Germany*
[5]*Fakultät für Physik, Universität Karlsruhe, 76131 Karlsruhe, Germany*
[6]*Department of Chemistry, University of California and LBNL, Berkeley, California 94720*

(Received 8 October 2001; published 19 December 2001)

The specific heat and thermal expansion of the same polycrystalline samples of $La_{0.65}Ca_{0.35}MnO_3$, with either ^{16}O or ^{18}O, have been measured for $85<T<310\,K$ in zero field and in magnetic fields to 60 kOe. Anomalies at $T_C(^{16}O)=265\,K$ and $T_C(^{18}O)=256\,K$ mark the zero-field ferromagnetic transitions. Their shapes, the derived changes in entropy and volume, and a comparison with the pressure dependence of T_C show that the ferromagnetic ordering is a thermodynamic first-order transition, broadened by a distribution in T_C. Magnetic fields change the character of the transition, broaden the anomalies, and shift them to higher temperatures. The shift is greater for ^{18}O than for ^{16}O, corresponding to a decrease in the isotope effect with increasing field.

DOI: 10.1103/PhysRevB.65.024441 PACS number(s): 75.30.Vn, 65.40.Ba, 65.40.De, 65.40.Gr

The magnetic and electrical properties of ‘‘colossal magnetoresistance’’ (CMR) materials were reported in 1950.[1] The double-exchange (DE) model was proposed the following year,[2] but recent attempts to explain the exceedingly large magnetoresistive changes in these oxide materials[3] led to the conclusion that the DE interaction must be augmented by an interaction between charge carriers and lattice distortions.[4] Such an interaction suggests the possibility of both a first-order transition at the Curie temperature (T_C), which would be very unusual for ferromagnetic ordering, and an isotope effect.[5,6] A thermodynamic analysis of thermal expansion (β) data,[7] based on a comparison with measurements, *made on other samples*, of the specific heat (C) and the dependence of T_C on pressure (P) has been interpreted as showing a second-order transition. Although there are other features that suggest first-order character,[8–10] they do not constitute thermodynamic proof of the nature of the transition, and it is frequently assumed that the transition is typical of ferromagnets and second order. The isotope effect has been observed[7,11,12] but its magnitude remains at issue. In this paper we report measurements of C and β for the *same, well-characterized* ^{16}O and ^{18}O samples of $La_{0.65}Ca_{0.35}MnO_3$ (LCMO). We show that in zero magnetic field [H] the transition at T_C is a slightly broadened first-order transition, with the broadening quantitatively accounted for by the random substitution of Ca on the La sites. With increasing H, there is a dramatic diminution in the isotope effect, for which there is no apparent theoretical explanation, and a shift and broadening of the anomalies in both $C(H)$ and $\beta(H)$, which, although also very unusual for ferromagnetic ordering, is in qualitative agreement with a polaron/bipolaron model.[13] In combination with low-T data, the C data suggest that a substantial fraction of the magnetic entropy is recovered only well above T_C, in agreement with the same model.[13]

The procedures for making the samples are similar to those used earlier by Franck *et al.*,[14] but with 12 sintering and regrinding steps. The density of the samples is 90% of the x-ray density. ^{18}O gas exchange was performed at 1200 °C, resulting in an ^{18}O concentration (by weight) of 91.3%. The larger samples, ~0.5–1 g, were used for zero-field continuous-heating measurements of C on ^{16}O and ^{18}O samples. A piece from an ^{16}O sample was used for similar measurements in fields to 70 kOe. These measurements were important in confirming the validity of in-field ac measurements and continuous-heating results on smaller samples. These smaller samples, ~100 mg, or pieces cut from them, were used for zero-field continuous-heating measurements of C for $85<T<300\,K$ and for ac measurements on 5-mg samples between 250 and 320 K in fields to 70 kOe. Pieces of these samples were also used for magnetization (M) measurements[14] and measurements of β (Ref. 15) that will be reported in more detail elsewhere. The ac measurements of C, which have high precision but inaccurate absolute values, were scaled by using the continuous-heating data on the same samples. Changes in the heating rate by a factor of 2 had no effect on the continuous-heating data, but in the vicinity of T_C the ac measurements did show an effect of sweep rate for $H\leq 2.5\,kOe$. That effect was probably associated with hysteresis, which can affect ac data at a first-order transition.[16] The measurements reported here were for sweep rates that gave results consistent with the continuous-heating data, implying that they correspond to thermal equilibrium.

Continuous-heating data for $C(0)$ and fits (see below) are shown in Fig. 1, and compared with $\beta(0)$, which closely mirrors the features in $C(0)$. The anomalies in C at T_C (taken to be the temperature of the maximum in C), unlike those associated with typical ferromagnetic (FM) transitions, are very nearly symmetric, although C is larger on the low-

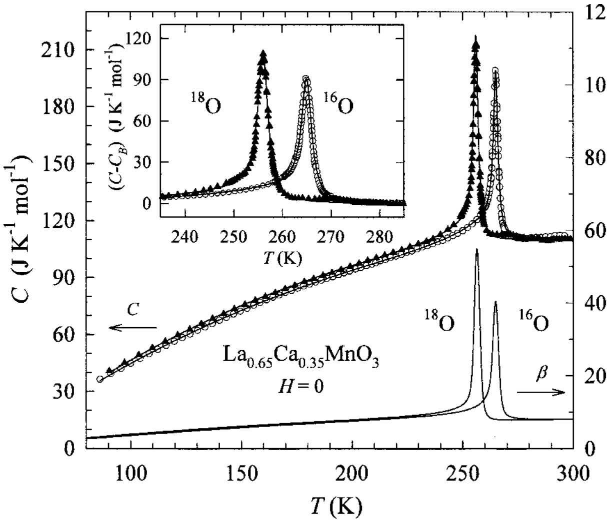

FIG. 1. Main graph: Zero-field specific heat (C) and linear thermal expansion (β) vs T for ^{16}O- and ^{18}O-doped La$_{0.65}$Ca$_{0.35}$MnO$_3$. Inset: $(C-C_B)$ vs T (see text). Only a fraction of the data is included. The curves through the C-data points are fits (see text).

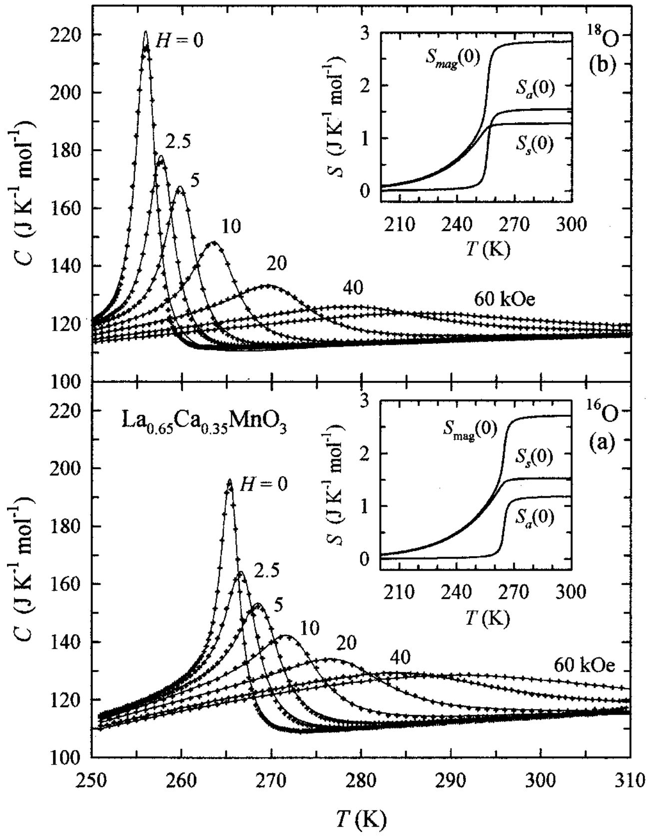

FIG. 2. Main graphs: C (ac data) vs T for $H=0-6$ T. Insets: Entropy vs T (see text for discussion).

temperature side than on the high-temperature side. They cannot be fitted with a model based on either critical or Gaussian fluctuations. However, their shapes do conform to expectations for a broadened first-order transition: a sharp peak, which corresponds to the latent heat $T\Delta S$, separating the different values of C, with their different T dependencies, for the two different phases.

To fit the data we assume that $C=C_B+C_{\rm mag}$; $C_{\rm mag}=C_a+C_s$, where C_B is a smoothly varying background term that corresponds to the lattice specific heat ($C_{\rm lat}$) plus possible small magnetic and electronic contributions; $C_{\rm mag}=C_a+C_s$ is the major "magnetic" contribution; C_a is the broadened latent-heat peak. C_s, which represents the difference in C between these two phases, is constrained to be zero well below T_C, rises to a maximum value at T_C, and is also broadened by the distribution in T_C. Over the temperature range $85<T<310$ K, C_B could be well represented by $C_B=B_0+B_1T+B_2T^2$. (Variations in the fitting expression for C_B by inclusion of harmonic-lattice[17] and/or spin-wave terms, and by changes in the interval of the fit, did not improve the fit.) C_a can be represented by either a Gaussian or a Lorentzian function. As the Lorentzian function was more tractable in the nonlinear least-squares fitting, the empirical representation $C_a=ab^2/(y^2+b^2)$ was chosen, where $y=(T/T_C-1)$, $a=$height, and $b=$the half width of the Lorentzian peak. A simple representation for the step in C at the transition is $C_s=d\exp(-f|y|)F(y/b)$, where d and f are parameters and $F(y/b)$ is a function reflecting the broadening. The eight parameters that appear in C are determined by fits to the data over the range $85<T<310$ K. (Similar fitting procedures were used for the zero-field thermal-expansion data and for the normalized ac specific-heat data for $H=0$.) The Lorentzian-broadened latent-heat term C_a has a half width ~1.5 K. This half width is roughly the same for samples ranging in size from ~5 to 1100 mg and comparable to the half width of the anomaly observed in single-crystal LCMO,[18] suggesting that the observed distribution in T_C is an intrinsic property. It can be accounted for by a random distribution of Ca in the sample: If the local T_C is determined by the average concentration of Ca in a domain of N unit cells, the observed half width and the variation of T_C with the overall concentration of Ca (Ref. 19) lead to an estimate of N of ~200, a value that is in good agreement with the results of Zuo and Tao.[20]

The pressure dependence of T_C (Ref. 21) can be used to test the anomalies in C and β, for consistency with the Clausius-Clapeyron equation for a first-order transition $dT_C/dP=\Delta V/\Delta S$. Since all the data were obtained on samples from the same batches, uncertainties that would otherwise arise from the strong sample dependence of the properties are avoided. The entropies of the Lorentzian part C_a of the ^{16}O and ^{18}O anomalies are, for $H=0$, $\Delta S=1.20$ and 1.56 J K^{-1} mol^{-1}, respectively (see Fig. 2). From the data for β, analyzed in the same way, $\Delta V=0.0131$ and 0.0195 cm^3 mol^{-1}, giving $dT_C/dP=10.9$ and 12.5 K GPa^{-1}, respectively. The corresponding experimental values[21] are 10.9 and 13.2 K GPa^{-1}, supporting the conclusion that the $H=0$ ferromagnetic ordering is a thermodynamic first-order transition. Zhao *et al.*[7] analyzed their data on β for an ^{16}O sample of La$_{0.67}$Ca$_{0.38}$MnO$_3$, together with data for C and dT_C/dP taken on other samples, with the Ehrenfest equation $dT_C/dP=3VT_C\Delta\beta/\Delta C$, and concluded that the ordering is an Ehrenfest second-order transition. Instead of taking the areas of the anomalies in C and β as measures of ΔS and ΔV

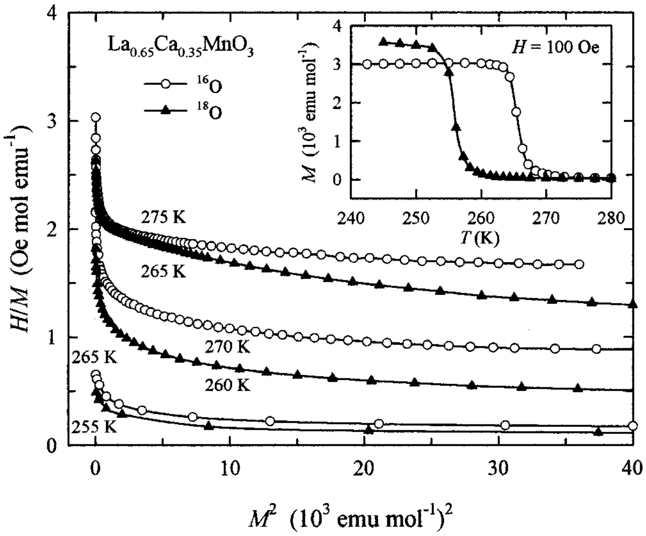

FIG. 3. Main graph: H/M vs M^2 for ^{16}O and ^{18}O samples from the *same batch* as the samples used in the C and β measurements. Inset: M vs T for $H=100$ Oe showing the sharp rise at T_C.

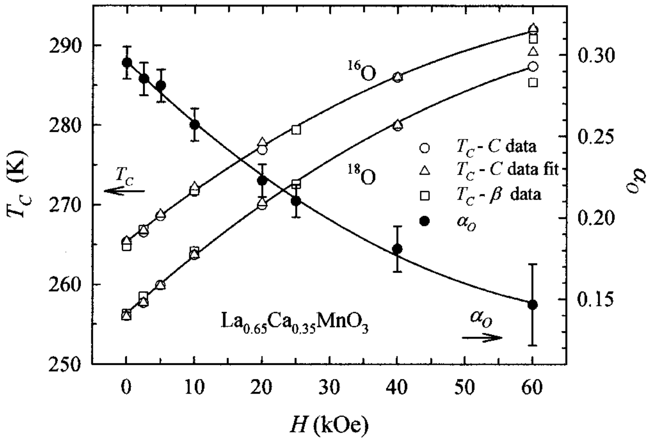

FIG. 4. $T_C(^{16}\mathrm{O})$, $T_C(^{18}\mathrm{O})$, and isotope exponent α_O vs H, where $T_C(^{16}\mathrm{O})$ and $T_C(^{18}\mathrm{O})$ are determined from the C and β data and from fits to C_a (see text). The values of α_O are the averages obtained from the C and β data. Curves through the points are guides for the eye.

at a first-order transition, they took the heights of the anomalies as ΔC and $\Delta\beta$ at a second-order transition. As expected on very general grounds, the anomalies in C and β are similar in shape and width. The heights are approximately proportional to the areas, ensuring that if ΔS and ΔV satisfy the Clapeyron equation, ΔC and $\Delta\beta$, when defined in that way, approximately satisfy the Ehrenfest equation. However, the shapes and widths of the anomalies in C are consistent with a first-order transition, for which there would be a sharp symmetric "peak" (the latent heat) and a "step" ΔC (the difference in C between the two phases); they are not consistent with an Ehrenfest second-order transition, for which there would be only the step. The data for C correspond to the sum of a temperature-dependent difference in C between the two phases and a latent heat, both broadened by the same distribution in T_C. ΔC contributes only $\sim$10% to the height of the anomaly; the major component of the anomaly is symmetric and inconsistent with the ΔC at a second-order transition. Similar considerations apply to the data for β. The evidence of hysteresis, which frequently accompanies first-order transitions but is not expected for continuous transitions, in the ac measurements of C for $H \leqslant \sim 2.5$ kOe, also suggests first-order character of the $H=0$ transition, which persists in low H. Several other measurements of $C(H)$ for ^{16}O samples of $\mathrm{La}_{(1-x)}\mathrm{Ca}_x\mathrm{MnO}_3$ $(0.3 \leqslant x \leqslant 0.4)$ (Refs. 18, 22, and 23) are qualitatively similar to those reported here, but are not suited for a quantitative discussion of the order of the phase transition, either because they are not absolute results,[18] or because there are insufficient data near T_C to reveal the symmetry of the anomaly.[22,23]

Measurements of M also give information on the nature of the transition: If the magnetic free energy (G) near T_C is written as $G=G_0+a_2(T-T_C)M^2+a_4M^4+\cdots$, a_4 cannot be negative if the transition is second order. Since the slope of H/M vs M^2 is $4a_4$, in this approximation, a test of the order of the transition can be obtained from such a plot.[9,10] H/M vs M^2 plots for small H are shown in Fig. 3. These results, similar to those reported in Ref. 9, have a negative slope, and thus support the conclusion that the transition is first order for zero and small fields. The sharp rise in M just below T_C, shown in the inset in Fig. 3, and similar results in electron-diffraction[20] and neutron-scattering[8] measurements, while not thermodynamic evidence, are more suggestive of a first-order transition than a continuous transition.

Using C_B obtained from the $H=0$ data, fits to $C_{\mathrm{mag}}(H) = [C(H)-C_B]$ were made for $H=2.5$, 5, 10, 20, 40, and 60 kOe. The ^{16}O and ^{18}O ac data and the fits are shown in Fig. 2. The fits provide a systematic procedure for obtaining the mean values of T_C, which correspond to the maxima in C_a, and their quality supports the general validity of the assumptions that underlie them. Perhaps the most striking property that reflects a sizable electron-phonon interaction is the large oxygen isotope effect ($\sim$10 K), usually observed in the magnetic transition in low field,[7,11,12] but also in the resistive transition, including high-field measurements.[12] The isotope effect in the thermodynamic transitions for C and β is evident in Figs. 1 and 2. The isotope exponent is given by $\alpha_O \equiv -d\ln(T_C)/d\ln(m_O)$, where m_O is the oxygen isotopic mass. α_O is $\sim$0.3 for $H=0$ and decreases significantly in higher fields. T_C values shown in Fig. 4 are obtained from the maxima in the C and β data, as well as from C_a. Values of T_C for 60 kOe show some scatter because the maxima in that field are poorly defined, and because the fitting function is less satisfactory when $H=60$ kOe. The general decrease in α_0 with H is unmistakable. The shape and field dependence of the anomalies in Figs. 1 and 2 are similar to the predictions of the Alexandrov and Bratkovsky bipolaron model,[13] which also predicts a possible first-order FM transition at T_C for $H=0$, and continuous transitions for larger fields. The T_C vs H results are quite similar to T_C vs P data obtained from pressure-dependent zero-field resistivity measurements[21] made on the same samples.

The specific-heat data make it possible to estimate $S_{\mathrm{mag}}(300)$, the magnetic entropy change from 0 to 300 K. Let $S_{\mathrm{mag}}(300)-S_{\mathrm{mag}}(200) \equiv S_a+S_s = \int C_a/T dT + \int C_s/T dT$, the magnetic entropy between 200 and 300 K. Plots of $S_a(0)$, $S_s(0)$, and $S_{\mathrm{mag}}(0)$ vs T for $H=0$ are shown as insets in Fig. 2. As can be seen from the insets, $S_{\mathrm{mag}}(300)-S_{\mathrm{mag}}(200)=2.75\pm0.05\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for both the ^{16}O and ^{18}O materials. Below ∼200 K C_B is indistinguishable from C. However, we can use the data of Fisher *et al.*[24] to make a rough estimate of $S_{\mathrm{mag}}(200)$. They find that for $1<T<12\,\mathrm{K}$ the electronic (γT) and spin-wave ($B_{\mathrm{fsw}}T^{3/2}$) contributions to C have $\gamma=4\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$ and $B_{\mathrm{fsw}}=0.7\,\mathrm{mJ\,K^{-5/2}\,mol^{-1}}$, and therefore $S_{\mathrm{mag}}(200)$ is ∼2 $\mathrm{J\,K^{-1}\,mol^{-1}}$. (The entropy associated with the anomaly in the lattice expansion at T_C is estimated to be ∼0.1 $\mathrm{J\,K^{-1}\,mol^{-1}}$, well within the overall uncertainty of the measurements.) Then $S_{\mathrm{mag}}(300)\sim4.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$, or ∼40% of 12.7 $\mathrm{J\,K^{-1}\,mol^{-1}}$, the entropy of the "free" Mn^{3+} (spin-2) and Mn^{4+} (spin-$\frac{3}{2}$) ions at high T. This result implies either that C_{lat} is considerably smaller than C_B,[25] or that ∼60% of the magnetic entropy in LCMO is removed above 300 K. This latter possibility is consistent with $\mathrm{Mn}^{4+}/\mathrm{Mn}^{3+}$ moments combining at temperatures well above T_C to form clusters,[26] FM inclusions,[27,28] polarons[28] and/or bipolarons,[13] or some combination of these, in dynamic equilibrium. For example, assume that 0.35 moles of $\mathrm{Mn}^{3+}/\mathrm{Mn}^{4+}$, randomly oriented at very high T, gradually combine, as T is lowered, to form 0.175 moles of FM bipolarons well above T_C. If either these bipolarons or the remaining 0.3 moles of Mn^{3+} (or some combination of the two) are progressively ordered as the temperature approaches 300 K, the reduction in entropy between very high T and 300 K is ∼8.7 $\mathrm{J\,K^{-1}\,mol^{-1}}$. The remaining ∼4 $\mathrm{J\,K^{-1}\,mol^{-1}}$ of entropy is sufficiently close to $S_{\mathrm{mag}}(300)\sim4.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$ to suggest that these interactions (or comparable ones) among the moments approximate what actually occurs in LCMO well above T_C. This picture is consistent with both the susceptibility and thermal-expansion measurements above T_C.[14,15] It is also consistent with the more rigorous and detailed discussion of the entropy for CMR materials by Alexandrov and Bratkovsky.[13]

The work at Amherst was supported by an Amherst College Faculty Research Grant. The work at the University of Alberta was supported by grants from the Natural Sciences and Engineering Research Council of Canada. The work at Lawrence Berkeley National Laboratory was supported by the Director, Office of Basic Energy Sciences, Materials Sciences Division of the U.S Department of Energy under Contract No. DE-AC03-76SF00098. C.M. and R.L. would like to thank W. Goldacker for the use of his magnet system.

---

[1] G. H. Jonker and J. H. Van Santen, Physica (Amsterdam) **16**, 337 (1950); **16**, 599 (1950).

[2] C. Zener, Phys. Rev. **82**, 403 (1951).

[3] R. von Helmolt *et al.*, Phys. Rev. Lett. **71**, 2331 (1994); M. McCormack *et al.*, Appl. Phys. Lett. **64**, 3045 (1994); S. Jin *et al.*, Science **264**, 413 (1994).

[4] A. J. Millis *et al.*, Phys. Rev. Lett. **74**, 5144 (1995).

[5] C. P. Bean and D. S. Rodbell, Phys. Rev. **126**, 104 (1962).

[6] J. B. Goodenough, J. Appl. Phys. **81**, 5330 (1997).

[7] G. Zhao *et al.*, Phys. Rev. Lett. **78**, 955 (1997).

[8] J. W. Lynn *et al.*, Phys. Rev. Lett. **76**, 4046 (1996).

[9] J. Mira *et al.*, Phys. Rev. B **60**, 2998 (1999).

[10] P. Novak *et al.*, Phys. Rev. B **60**, 6655 (1999).

[11] G. Zhao *et al.*, Nature (London) **381**, 676 (1996).

[12] J. P. Franck *et al.*, Phys. Rev. B **58**, 5189 (1998).

[13] A. S. Alexandrov and A. M. Bratkovsky, J. Phys.: Condens. Matter **11**, 1989 (1999).

[14] J. P. Franck *et al.* (unpublished).

[15] R. Lortz *et al.* (unpublished).

[16] W. Xin *et al.*, Phys. Rev. B **45**, 5131 (1992).

[17] J. E. Gordon *et al.*, Solid State Commun. **69**, 625 (1989).

[18] P. Lin *et al.*, J. Appl. Phys. **87**, 5825 (2000).

[19] P. Schiffer *et al.*, Phys. Rev. Lett. **75**, 3336 (1995).

[20] J. M. Zuo and J. Tao, Phys. Rev. B **63**, 060407(R) (2001).

[21] B. Lorenz *et al.*, *Science and Technology of High Pressure*, Proceedings of the 17th International Conference on High Pressure Science and Technology, edited by M. H. Manghnani *et al.* (Hyderabad Universities, Hyderabad, India, 2000), Vol. II, p. 705.

[22] S. H. Park *et al.*, Phys. Rev. B **56**, 67 (1997).

[23] X. Bohigas *et al.*, J. Magn. Magn. Mater. **208**, 85 (2000).

[24] R. A. Fisher *et al.*, Phys. Rev. B **64**, 134425 (2001).

[25] J. E. Gordon *et al.*, Phys. Rev. B **59**, 127 (1999).

[26] J. Tanaka *et al.*, J. Phys. (France) Lett. **44**, L129 (1983).

[27] A. Moreo *et al.*, Science **283**, 2034 (1999).

[28] J. M. De Teresa *et al.*, Nature (London) **386**, 256 (1997).