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Article in *Journal of Applied Physics* · June 2002

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Tuning of the magnetocaloric effect in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_{3-\delta}$ nanoparticles synthesized by sol-gel techniques

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(Received 30 January 2002; accepted for publication 18 March 2002)

We report the effect of progressive reduction of the annealing temperature on the magnetocaloric effect (MCE) of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_{3-\delta}$ nanoparticles synthesized by the sol-gel technique. With this method, we are able to obtain particle diameters ranging from 60 to 500 nm. The peak in the MCE at the ferromagnetic to paramagnetic phase transition is strongly reduced as annealing temperature does, due to loss of the intrinsic first-order magnetic phase transition. This opens up a new way in which to tune the intrinsic properties of mixed-valence manganites, most of which are associated with the first-order character of the magnetic transition. © 2002 American Institute of Physics. [DOI: 10.1063/1.1476972]

I. INTRODUCTION

The intrinsic properties of mixed valence manganites have been a subject of attention since the rediscovery of colossal magnetoresistance nearly 10 years ago.¹ These materials have demonstrated a great variety of phenomenology that has been clearly linked to several theoretical proposals. First was colossal magnetoresistance,^{1,2} and later giant thermal expansion,³ the isotopic effect,⁴ and charge ordering structures.⁵ As a theoretical approach, a parallel effort has led to leaving behind the early double exchange theories;^{6,7} spin-phonon coupling⁸ or percolation of phase separated regions^{9,10} now provide a more accurate prediction of experimental data.

However, much has to be done before one can consider this field of investigation closed. One unresolved issue at the moment is the nature of the magnetic phase transition in manganites and its relationship with their physical properties. For example, in the optimally doped compound $\text{A}_{2/3}\text{B}_{1/3}\text{MnO}_3$ it has been found that the ferromagnetic-paramagnetic phase transition is of first order for (La, Ca),¹¹ but of second order for (La, Sr).^{11,12} This change in the nature of the magnetic phase transition is followed by a corresponding change in the physical properties of the compound. For example, colossal magnetoresistance, thermal expansion, the magnetocaloric effect, and the isotopic effect are reduced in the case of second-order transitions.^{4,13,14} This change has been tentatively related to a different crystalline structure in samples with different kinds of magnetic phase transitions.¹⁴

In this work we will show how a similar change in the character of the magnetic phase transition can be achieved by keeping the cation and the doping level unchanged, but con-

trolling the grain size and, simultaneously, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio via oxygen vacancies. The intrinsic first-order magnetic transition can be minimized and eventually evolves towards a second-order one as the grain size diminishes. This provides a new tool with which to control the physical properties associated with the transition. The magnetocaloric effect, in particular, is closely related to the type of transition, and its change is a perfect test by which to see this evolution.

II. EXPERIMENT

Nanometric particles were prepared by the sol-gel technique. We have used an aqueous solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ of stoichiometric proportions and urea as the gelificant agent in a fixed concentration ($[\text{urea}]/[\text{La}^{3+}] + [\text{Ca}^{2+}] + [\text{Mn}^{2+}] = 10$). This solution is slowly evaporated at temperatures ranging from 75 to 137 °C (the melting point of urea). Upon cooling, a gel is formed, and later it is decomposed by heating it at 250 °C for 3 h, yielding the precursor with which to prepare the final samples. This precursor is annealed at different temperatures up to 1100 °C for 6 h. This procedure and several related results of it have been described in earlier articles.^{15,16} The particle diameter (D) was measured by scanning electron microscopy (SEM). Through x-ray diffraction we detected high crystallinity and the absence of spurious phases for samples annealed at $T \geq 700$ °C.

We prepared samples with sintering temperatures ranging from 700 to 1100 °C with an interval of 100 °C. This leads to a series of increasing mean particle sizes of 60 ± 10 , 95 ± 14 , 150 ± 21 , 250 ± 38 , and 500 ± 95 nm, respectively. The oxygen content was checked by iodometric titrations. The percentage of Mn^{4+} was found to increase from the stoichiometric value for the high temperature treated samples to nearly 40% for the lowest temperature ones. This is probably mainly due to the loss of oxygen content (an

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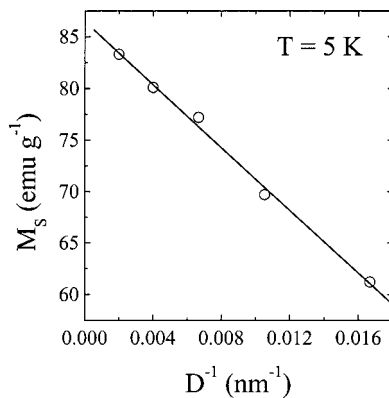


FIG. 1. Linear relationship between the saturation magnetization ($T=5$ K) and the surface/volume ratio of the particles (D^{-1}).

increase in the δ factor), or more accurately, to an increase in cationic vacancies as the sintering temperature is lowered.

The initial magnetization curves were measured using a vibrating sample magnetometer from 160 to 330 K in fields up to 10 kOe.

III. RESULTS AND DISCUSSION

The magnetic properties of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ nanoparticles have previously been studied.^{16,17} It has been shown that the temperature at which the ferromagnetic to paramagnetic phase transition takes place (T_C) does not depend on the grain size.^{17–19} It remains almost unchanged at a value of around 260 K. However, the saturation magnetization at low temperatures scales linearly with D^{-1} , that is, with the surface/volume ratio of the particles (see Fig. 1). This dependence is a clear signal that the degree of crystallinity is the same for all the samples studied. The reduction in magnetization is only a function of the particle size so the presence of a magnetic “dead” layer is approximately the same for all the samples. Of course, it is more important in the smaller grain size samples, since the surface contribution is larger in that case. The cationic vacancies and the defects in the structure are mainly located in this external zone, and lead to a reduction of ferromagnetic interaction. In general, each particle can be seen as being composed of two different parts. The inner part is a core where double exchange interaction dominates and promotes ferromagnetic behavior. The outer part is a layer where magnetic interactions are clearly modified by defects, vacancies, stress, and broken bonds directing to a disordered magnetic state.^{20–22}

With the objective of testing the effect of the grain size in the magnetic phase transition we have measured initial magnetization curves in fields up to 10 kOe in the entire series of samples. In Fig. 2 we can observe the initial magnetization curves for the two extreme samples studied (those with grain size of 60 and 500 nm). The two results are clearly different. In the first case, the isotherms are almost equally spaced and it is difficult to distinguish the critical point. However, in the sample annealed at higher temperature (the 500 nm sample), the critical region can clearly be differentiated. Moreover, some of the curves exhibit a kink that is commonly associated with first-order magnetic transi-

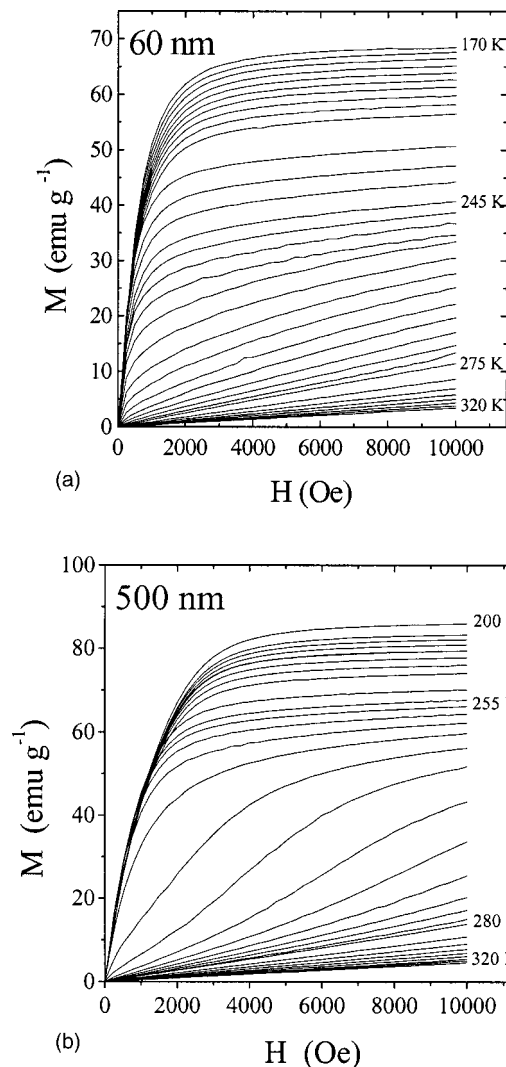


FIG. 2. (a) Initial magnetization isotherms of a sol-gel sample with a grain size of 60 nm. The temperature measurements are at intervals of 170–245 K ($\Delta T=5$ K); 245–275 K ($\Delta T=2$ K); 275–320 K ($\Delta T=5$ K). (b) Initial magnetization isotherms of an annealed sol-gel sample with a particle size of 500 nm. Temperature measurements are at intervals of 200–255 K ($\Delta T=5$ K); 255–280 K ($\Delta T=2$ K); 280–320 K ($\Delta T=5$ K). We can clearly observe the bend in the curves around the critical temperature that denotes a first-order magnetic phase transition.

tions. However, this is only a qualitative inspection. In order to check the nature of the magnetic transitions we have used the Banerjee criterion.^{11,23} By plotting H/M vs M^2 in the critical region, the slope of the resulting curves denotes whether a magnetic transition is of first or second order. From a thermodynamic point of view it can be deduced that, if all the curves have a positive slope, the magnetic transition is of second order. On the other hand, if some of the curves show a negative slope at some point, the transition is of first order. In the case of the smallest grain size sample, as we can see from the slopes of the different isotherms, a second-order transition occurs. For the opposite case shown on the right in Fig. 3 the bigger grain size sample, some of the curves show a negative slope, which is the sign of a first-order magnetic phase transition [see Figs. 3(a) and 3(c)]. For the intermediate samples, the first-order character is present. However, in the sample with particle size of 95 nm, for example, although

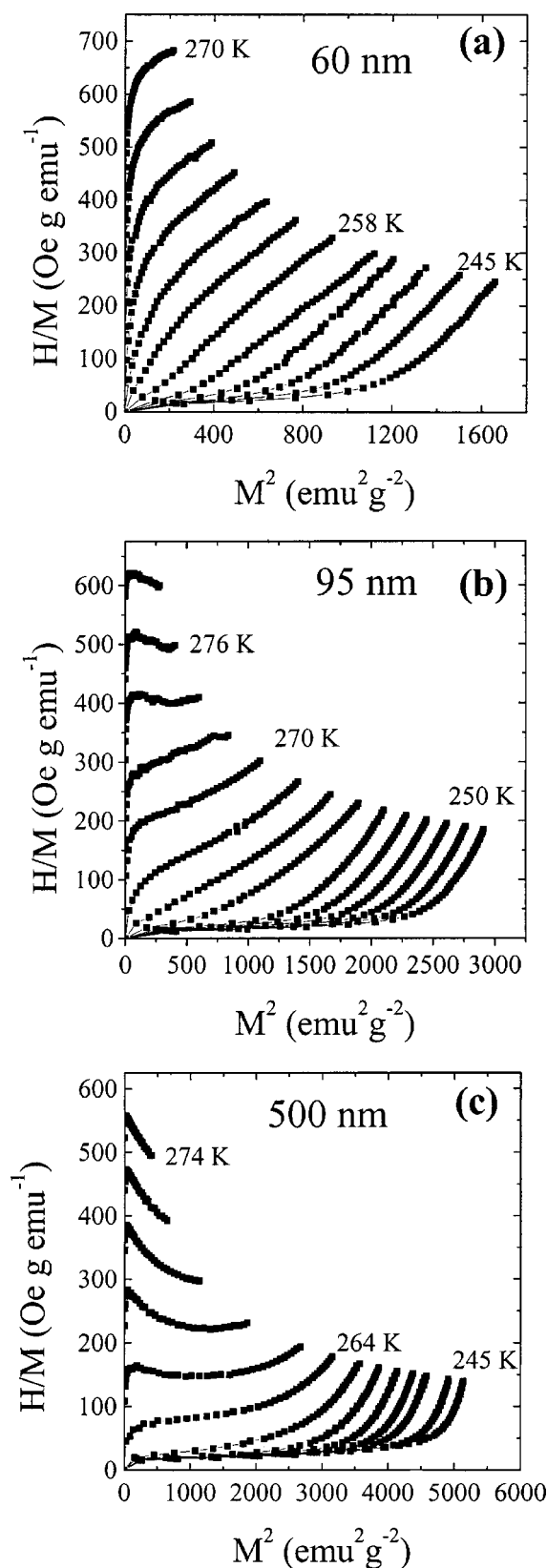


FIG. 3. (a) Banerjee plot of the sample with particle size of 60 nm. All the curves have a positive slope. This is a slight sign of a second-order phase transition. (b) Banerjee plot of a sample with particle size of 95 nm. The indication of a first-order transition through the negative slope in the curves is very soft. (c) Banerjee plot of a sample with particle size of 500 nm. Some of the curves show a negative slope. Thus the magnetic phase transition in this case is a first-order one. In all cases, the temperature intervals are the same as those in Fig. 2.

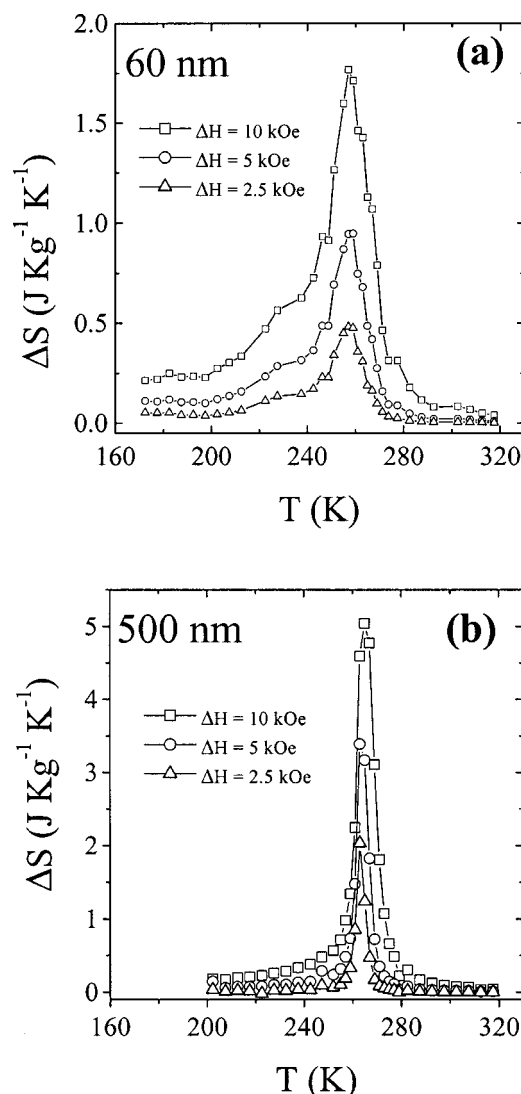


FIG. 4. (a) Magnetocaloric effect for different applied magnetic fields for a sample with particle size of 60 nm. (b) Magnetocaloric effect for the sample with particle size of 500 nm.

there, it is difficult to discern the negative slope in Fig. 3(b). This can be interpreted as a sign that the transition convolutes into a second-order one as the grain size diminishes. It seems that below a certain limit (in our case around 95 nm) the transition can no longer behave as a first-order one.

This can be understood by taking into account a model with particle differences in the inner core and outer layer. The center part always retains the intrinsic first-order magnetic transition of the bulk compound. However, the disordered outer layer is more likely to undergo a second-order transition, from the disordered state into the paramagnetic, as has previously been noticed indirectly.²² The composition of both transitions hides the presence of the first-order one. In this way, the overall result in the smallest particles is a second-order transition, although both contributions should be present at the same time. This is a very interesting result, because we are able to change the nature of an intrinsic property of a material (like the magnetic phase transition) by changing the particle size and the oxygen vacancies.

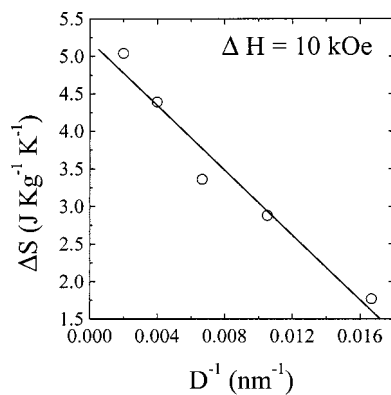


FIG. 5. Linear relationship between the magnetocaloric effect ($\Delta H = 10$ kOe) and the surface/volume ratio of the particles (D^{-1}).

As a result of this evolution in the magnetic phase transition, some of the properties related to it are also modified in a similar way. One of them is the magnetocaloric effect (MCE), that is, the magnetic entropy change (ΔS_M) in the phase transition produced by changes in the magnetic field applied to the system. This is only a consequence of minimizing the transition as the grain size is made smaller. As we were able to see from the theoretical formulation, both properties are related.

The basis of the relationship between magnetic measurements and the change in entropy is the Maxwell equation:²⁴

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H. \quad (1)$$

Integrating and making an approximation suitable for discrete measurements, we obtain²⁵

$$|\Delta S_M| = \sum \frac{(M_n - M_{n+1})_H}{T_{n+1} - T_n} \Delta H_n, \quad (2)$$

where M_n and M_{n+1} are the magnetization values measured in magnetic field H at temperatures T_n and T_{n+1} , respectively.

The magnetocaloric effect presents a variation that is also proportional to the grain size. It is known that continuum second-order phase transitions show a smaller effect than first-order ones. Their gentle decrease in magnetization close to the transition leads to a less pronounced peak of the MCE. As we can see in Fig. 4, the MCE peak is much higher and narrower for the 500 nm sample than for the 60 nm one. The change in the magnitude of the effect with the surface/volume ratio can be seen in Fig. 5. Clear again is the progressive increase of the MCE as the contribution of the outer magnetically disordered layer of each particle diminishes. This result is related to the progressive continuous change in the order of the transition, which is the basic effect that underlies and governs the MCE.

Finally, we can try to relate the result obtained in magnetic characterization of the samples to others related to the dc resistivity and the intrinsic colossal magnetoresistance. As was already demonstrated in a previous paper,¹⁷ the CMR peak can also be tuned by means of the particle size. The relationship between both effects is neither evident nor di-

rect, but they seem to be related in some way. When the particle size is decreased, intrinsic CMR follows the same tendency and, eventually, disappears. A similar result was presented here for the MCE. Both results are associated with the presence of the outer magnetically disordered layer in the particles. Its great effect progressively hides the intrinsic properties of mixed-valence manganites. They are present, but significantly diminished as the extrinsic contribution grows.

IV. CONCLUSIONS

In this article we have studied the ferromagnetic to paramagnetic phase transition in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ nanoparticles. For the biggest particles, the transition is a first-order one, just like in ceramic materials with grains in the micrometer range. However, as the particle size diminishes (and the contribution from a magnetically disordered outer layer increases), the transition becomes more gradual and, for the smallest particles produced (those around 60 nm), the transition becomes a second-order one. The magnetocaloric effect, which is closely related to the steep of the magnetic phase transition, follows the same trend. Its value is reduced in an almost linear way as the surface/volume ratio of the particles increases.

ACKNOWLEDGMENTS

The authors want to acknowledge Dr. R. D. Sánchez for stimulating discussions. One of the authors (L.E.H) wants to thank MCyT of Spain for a Ph.D. fellowship. This work was developed as part of Project No. MAT2001-3749, DGI, MCyT, Spain.

- ¹R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Sanwer, *Phys. Rev. Lett.* **71**, 2331 (1993).
- ²S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, *Science* **264**, 413 (1994).
- ³M. R. Ibarra, P. A. Algarabel, C. Marquina, J. Blasco, and J. García, *Phys. Rev. Lett.* **75**, 3541 (1995).
- ⁴G. Zhao, K. Conder, H. Keller, and K. A. Muller, *Nature (London)* **381**, 676 (1996).
- ⁵S. Mori, C. H. Chen, and S.-W. Cheong, *Nature (London)* **392**, 473 (1998).
- ⁶C. Zener, *Phys. Rev.* **82**, 403 (1951).
- ⁷P. G. de Gennes, *Phys. Rev.* **118**, 141 (1960).
- ⁸A. J. Millis, P. B. Littlewood, and B. I. Shraiman, *Phys. Rev. Lett.* **74**, 5144 (1995).
- ⁹M. Uehara, S. Mori, C. H. Chen, and S.-W. Cheong, *Nature (London)* **399**, 560 (1999).
- ¹⁰M. Mayr, A. Moreo, J. A. Vergés, J. Arispe, A. Feiguin, and E. Dagotto, *Phys. Rev. Lett.* **86**, 135 (2001).
- ¹¹J. Mira, J. Rivas, F. Rivadulla, C. Vázquez-Vázquez, and M. A. López-Quintela, *Phys. Rev. B* **60**, 2998 (1999).
- ¹²S. E. Lofland, V. Ray, P. H. Kim, S. M. Bhagat, M. A. Mannheimer, and S. D. Tyagi, *Phys. Rev. B* **55**, 2749 (1997).
- ¹³For a review of intrinsic properties of manganites, see, for example, J. M. D. Coey, M. Viret, and S. von Molnar, *Adv. Phys.* **48**, 167 (1999).
- ¹⁴J. Mira, J. Rivas, L. E. Hueso, F. Rivadulla, M. A. López-Quintela, M. A. Señaris-Rodríguez, and C. A. Ramos, *Phys. Rev. B* **65**, 024418 (2002).
- ¹⁵C. Vázquez-Vázquez, M. C. Blanco, M. A. López-Quintela, R. D. Sánchez, J. Rivas, and S. B. Oseroff, *J. Mater. Chem.* **8**, 991 (1998).
- ¹⁶J. Rivas, L. E. Hueso, A. Fondado, F. Rivadulla, and M. A. López-Quintela, *J. Magn. Magn. Mater.* **221**, 57 (2000).
- ¹⁷L. E. Hueso, J. Rivas, F. Rivadulla, and M. A. López-Quintela, *J. Appl. Phys.* **86**, 3881 (1999).

- ¹⁸N. Zhang, W. Ding, W. Zhong, D. Xing, and Y. Du, Phys. Rev. B **56**, 8138 (1997).
- ¹⁹A. K. M. Akther Hossain, L. F. Cohen, F. Damay, A. Berenov, J. MacManus-Driscoll, N. McN. Alford, N. D. Mathur, M. G. Blamire, and J. E. Evetts, J. Magn. Magn. Mater. **192**, 263 (1999).
- ²⁰J. M. D. Coey, Phys. Rev. Lett. **27**, 1140 (1971).
- ²¹R. H. Kodama, A. E. Berkowitz, E. J. McNiff, Jr., and S. Foner, Phys. Rev. Lett. **77**, 394 (1996).
- ²²J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, Phys. Rev. Lett. **81**, 1953 (1998).
- ²³S. K. Banerjee, Phys. Lett. **12**, 16 (1964).
- ²⁴H. B. Callen, *Thermodynamics* (Wiley, New York, 1981).
- ²⁵A. M. Tishin, in *Handbook of Magnetic Materials*, edited by K. H. J. Buschow (Elsevier, Amsterdam, 1999), Vol. 12.