Giant magneto-caloric effect around room temperature at moderate low field variation in La$_{0.7}$(Ca$_{1−x}$Sr$_x$)$_{0.3}$MnO$_3$ perovskites

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ABSTRACT

Among the perovskite manganites, a series of La$_{1−x}$Ca$_x$MnO$_3$ has the largest magneto-caloric effect (MCE) ($|\Delta S_m|_{max} = 3.2$–6.7 J/kg K at $\Delta H = 13.5$ kOe), but the Curie temperatures, T_C, are quite low (165–270 K). The system of LaSrMnO$_3$ has quite high T_C but its MCE is not so large. The manganites La$_{0.7}$(Ca$_{1−x}$Sr$_x$)$_{0.3}$MnO$_3$ ($x = 0$, 0.05, 0.10, 0.15, 0.20, 0.25) have been prepared by solid state reaction technique with an expectation of large MCE at room temperature region. The samples are of single phase with orthorhombic structure. The lattice parameters as well as the volume of unit cell are continuously increased with the increase of x due to large Sr^{2+} ions substituted for smaller Ca^{2+} ions. The field-cooled (FC) and zero-field-cooled (ZFC) thermomagnetic measurements at low field and low temperatures indicate that there is a spin-glass like (or cluster glass) state occurred. The Curie temperature T_C increases continuously from 258 K (for $x = 0$) to 293 K (for $x = 0.25$). A large MCE of 5 J/kg K has been observed around 293 K at the magnetic field change $\Delta H = 13.5$ kOe for the sample $x = 0.25$. The studied samples can be considered as giant magneto-caloric materials, which is an excellent candidate for magnetic refrigeration at room temperature region.

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1. Introduction

The conventional thermo-mechanical cooling techniques, through expansion and gas liquefaction can be improved by magnetic systems. The magnetic system can reduce the size of the refrigerators, making them more effective and more cleaner. The magnetic refrigerators are based on the magneto-caloric effect (MCE) [1,2], the temperature change of magnetic material, associated with an external magnetic field change in an adiabatic process, is defined as the magneto-caloric effect. The magneto-caloric effect has been used for many years to achieve low temperatures (of the order of milikelvins) through adiabatic demagnetization of paramagnetic salts. Magnetic materials with giant magneto-caloric effect (GMCE) have attracted growing interests owing to their excellent performance for the magnetic refrigeration technique [3,4]. In most cases, however, a high cooling efficiency can only be achieved in a magnetic field change as high as $\Delta H = 50$ kOe, which severely limits the household application of magnetic refrigeration. It is therefore of significant

importance to search for magnetic materials that can display large MCE in a lower field of less than 15 kOe and in a wide temperature range. With these materials, the magnetic refrigerator can operate effectively under a field that can be generated by permanent magnets. In the last few years a large magnetic entropy ($|\Delta S_m|$) has been discovered in ceramic manganites (A$_{1−x}$A′$_x$ MnO$_3$ with A = La and A′ = Ca, Sr, Gd, etc.) [5–8] and many researchers have published a large number of papers regarding with large MCE in different perovskites for example in cobaltite [9], in Ni, Cu and Co doped-LaSr manganites [10–14], in LaPb manganites [15], in LaCd manganites [16], in PrPb manganites [17,18] and in LaPrPb manganites [19]. Among the perovskite manganites, a series of La$_{1−x}$Ca$_x$MnO$_3$ has the largest MCE, namely $|\Delta S_m|_{max} = 5.50$ J/kg K at $T_C = 230$ K and $\Delta H = 15$ kOe for La$_{0.8}$Ca$_{0.2}$MnO$_3$ [19], $|\Delta S_m|_{max} = 5.00$ J/kg K at $T_C = 260$ K and $\Delta H = 10$ kOe for La$_{0.67}$Ca$_{0.33}$MnO$_{3−\delta}$ [20], $|\Delta S_m|_{max} = 6.40$ J/kg K at $T_C = 267$ K and $\Delta H = 30$ kOe for La$_{3/2}$Ca$_{1/3}$MnO$_3$ [21], the largest MCE, $|\Delta S_m|_{max} = 3.2$–6.7 J/kg K at quite low $T_C = 165$–270 K and $\Delta H = 13.5$ kOe have been reported [22]. The system of LaSrMnO$_3$ has quite high T_C but its MCE is not so large [23]. Similar to LaSrMnO$_3$, another system of manganites La$_{1−x}$Pb$_x$MnO$_3$ has quite high T_C (235–360 K) but its MCE is not so large (0.65–1.35 J/kg K at $\Delta H = 13.5$ kOe) [15]. We hope that the mixing of LaCaMnO$_3$ and

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LaSrMnO$_3$ should give high enough value of $|\Delta S_m|_{max}$ at near room temperature region. This report presents our study of structure, magnetic and magneto-caloric properties of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$ MnO$_3$ perovskistes.

The magnetic entropy can be measured through either the adiabatic change of temperature by the application of a magnetic field, or through the measurement of classical $M(H)$ isotherms at different temperature [24]. We used the second method to avoid the difficulty of adiabatic measurements. The variation of magnetic entropy and $M(H)$ isotherms are related by the thermodynamic Maxwell relation [2]

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

From Eq. (1), the isothermal entropy change can be calculated by means of magnetic measurements

$$\Delta S_M(T,H) = S_M(T,H) - S_M(T,0) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \tag{2}$$

For magnetization measurements made at discrete field and different temperatures, Eq. (2) can be approximated by

$$|\Delta S| = \sum \frac{(M_n - M_{n+1})_H}{T_{n+1} - T_n} \Delta H_n \tag{3}$$

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

2. Experiments

La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ ($x = 0.00$; 0.05; 0.10; 0.15; 0.20 and 0.25) manganites were prepared by using a standard ceramic technology. Stoichiometric mixture of La$_2$O$_3$, SrCO$_3$, MnCO$_3$, CaCO$_3$ were ground, pressed and heated in air several times with intermediate grinding. The samples were presintered at 900 °C for 5 h and sintered at 1200 °C for 15 h. The structure of the samples was examined by X-ray diffractometer Bruker D5005. The microstructure and chemical composition were studied using a 5410 LV Jeol scanning electron microscope (SEM) which includes an energy dispersion spectrometer (EDS). Magnetic measurements were performed using a vibrating sample magnetometer (VSM) DMS 880 Digital Measurement System in magnetic field up to 13.5 kOe.

3. Results and discussion

Fig. 1 shows a SEM image of a representative sample $x = 0.05$. It can be seen that the crystallites are of small size ($\square$ 0.5 μm) and homogeneous. The microstructure observation performed for the rest samples indicated that the grain size remained almost unchanged from this sample to another one. The XRD patterns shown in Fig. 2 reveals that the La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ samples are of single phase with an orthorhombic perovskite structure and with no impurities detected. The lattice parameter of samples are derived from their corresponding XRD patterns and presented in Table 1. In this series of samples, the average ionic radius of the A site $\langle r_A \rangle$ (A = La, Ca, Sr) is systematically increased from sample $x = 0.00$ to sample $x = 0.25$ due to substitution of Ca^{2+} ($\langle r_{Ca}^{2+} \rangle = 1.14$ Å) by the larger Sr^{2+} ($\langle r_{Sr}^{2+} \rangle = 1.32$ Å), therefore the lattice parameters as well as volume of unit cell increased with increasing x. However, no structural phase transition which is related to increasing $\langle r_A \rangle$ has been found in this system. Fig. 3 shows an example of isothermal magnetization curves for one of the members of the series with a field step 500 Oe in a range 0–13.5 kOe and a temperature interval of 5 K in a range of
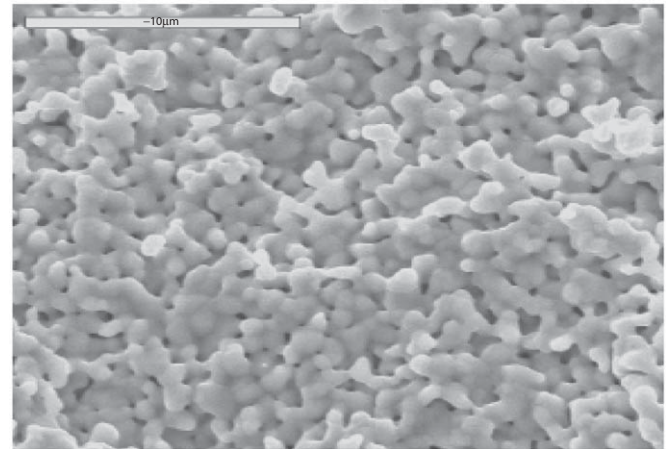

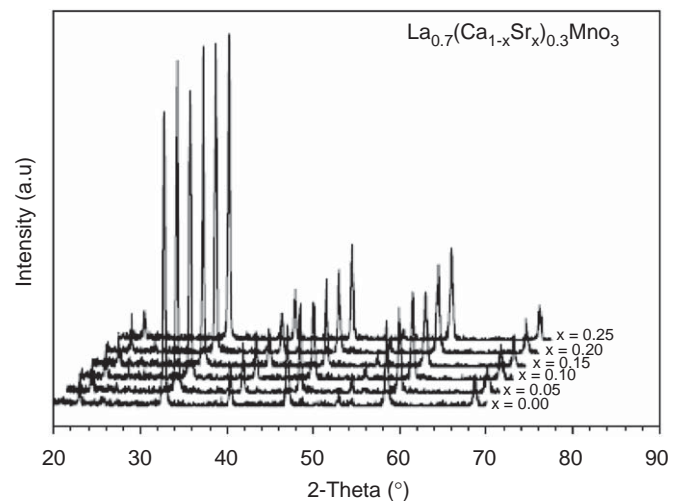**Fig. 1.** Microstructure of sample La$_{0.7}$(Ca$_{0.95}$Sr$_{0.05}$)$_{0.3}$MnO$_3$.

Fig. 2. X-ray diffraction patterns of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ samples.

Table 1
Lattice parameter of samples La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$.

Sample	$x = 0$	0.05	0.10	0.15	0.20	0.25
a (Å)	5.4606	5.4610	5.4613	5.4616	5.4619	5.4623
b (Å)	5.4619	5.4629	5.4633	5.4636	5.4643	5.4647
c (Å)	7.7270	7.7285	7.7292	7.7297	7.7303	7.7308
$V_{unit\ cell}$ (Å)	230.46	230.56	230.60	230.65	230.71	230.76
T_C (K)	258	263	268	275	282	293
$|\Delta S_m|_{max}$ (J/kg K)	6.5	0.62	3.62	1.65	1.81	5

temperatures around T_C. To ensure the measurements of the figure, only some of isotherms are presented in Fig. 3 for a representative sample of La$_{0.7}$Ca$_{0.225}$ Sr$_{0.075}$MnO$_3$. From this figure it can be explained that there is a strongly purgative change of the magnetization around T_C indicating a large magnetic entropy change. Another feature to be examined is that a large proportion of changes of the magnetization occur in a relative low-field range which is advantageous for the household application of MCE materials. Fig. 4 shows the temperature dependence of magnetization of La$_{0.7}$(Ca$_{1-x}$Sr$_x$)$_{0.3}$MnO$_3$ samples measured in a low applied field of 20 Oe under both field cooling (FC) and zero-field cooling (ZFC). The Curie temperature T_C is determined from the Arrott plots and it has been shown that the T_C is 258 K (for $x = 0.00$), 263 K (for $x = 0.05$), 268 K (for $x = 0.10$), 275 K (for
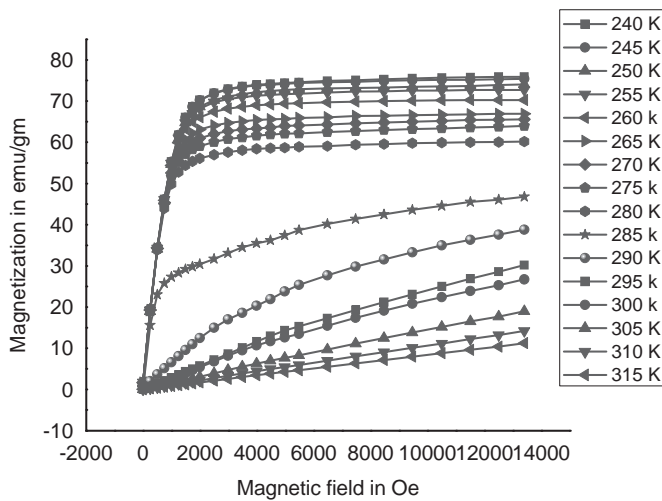
Fig. 3. Magnetization as function of magnetic field at different temperature of samples $La_{0.7}(Ca_{0.95}Sr_{0.05})_{0.3}MnO_3$.

Fig. 5. The magnetic entropy change as a function of temperature for the samples $x = 0.00$, 0.10 and 0.25.
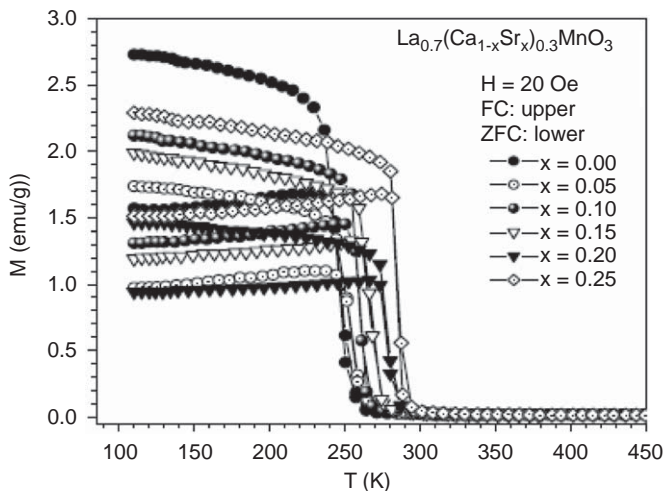
Fig. 4. Field-cooled (FC) and zero-field-cooled (ZFC) thermo-magnetic curves of $La_{0.7}(Ca_{1-x}Sr_x)_{0.3}MnO_3$ samples.

$x = 0.15$), 282 K (for $x = 0.20$) and 293 K (for $x = 0.25$), respectively. While Sr^{2+} substituted for Ca^{2+} in the samples, the ratio Mn^{4+}/Mn^{3+} unchanged therefore the increase of T_C on x could be explained by the enhancement of double exchange interaction due to the strengthening of $\langle r_A \rangle$ [25]. One can see from Fig. 4 that the FC and ZFC curves of samples are separated from each other at low temperatures. Below Curie temperature magnetization of the sample decreases with decreasing temperature, i.e. in this region the predominant anti-ferromagnetic phase coexists and competes with the ferromagnetic phase at low temperatures. The role of grain boundary and grain surface could be a reason of such phenomenon. At grain boundary, exchange interactions (super exchange and double exchange) are weak compared to those inside the grain. This leads to the inhomogeneity of magnitude of exchange interaction. In addition, crystal structure at grain boundary is often distorted, only short-range order remains and structure is similar to spin glass, leading to frustration feature to occur easily [26]. Fig. 5 shows the magnetic entropy change as a function of temperature for the samples $x = 0.00$, 0.10 and 0.25 at $\Delta H = 13.5$ kOe. Obviously, $|\Delta S_m|$ has reached the largest value of 6.5 J/kg K for sample $x = 0.00$ at 260 K and 5 J/kg K for sample $x = 0.25$ at 293 K in magnetic field variation of $\Delta H = 13.5$ kOe. The
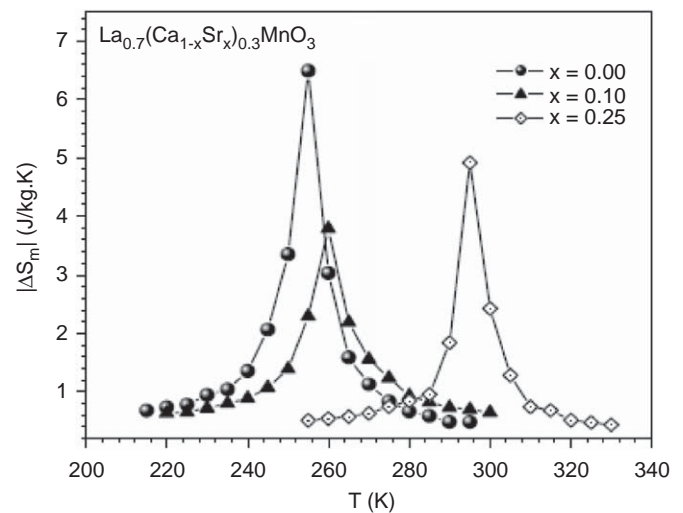
value of $|\Delta S_m|_{max}$ obtained in the present work is better than that obtained for pure Gd at room temperature (4.2 J/kg K in $\Delta H = 1.5$ T) [27]. Therefore the composition $x = 0.00$, 0.10, 0.25 could be considered as the good candidates for magnetic refrigerant working in sub-room temperature range, because of:

(1) a well-defined transition temperature due to sharp shape of $|\Delta S_m|$ (T) curve,
(2) a modest magnetic entropy change upon application/removal of a low magnetic field and easily controllable magnetic entropy,
(3) good chemical stability and with quite high efficiency ($\sim$60%), and,
(4) the possibility of being manufactured at a low price. From our study it is seen that the perovskites are polycrystalline. A large value of entropy change could be expected in single crystalline samples. Perovskites are easy to prepare and exhibit higher chemical stability as well as higher resistivity that are favorable for lowering eddy current heating. Beside these, since the Curie temperature of perovskite manganites is doping dependent, a large entropy change could be turned from low temperature to near and above room temperature, which is beneficial for operating magnetic refrigeration at various temperatures. The large magnetic entropy change in our samples must have originated from the considerable variation of magnetization near T_C. Moreover, it provides insight into the role of spin–lattice coupling in the magnetic ordering process.

4. Conclusions

In conclusion, the manganites $La_{0.7}(Ca_{1-x}Sr_x)_{0.3}MnO_3$ were prepared with single-phase orthorhombic structure. A detailed study of the magneto-caloric effect in the $La_{0.7}(Ca_{1-x}Sr_x)_{0.3}MnO_3$ compounds has been investigated. We have found the large magnetic entropy changes, i.e. the large magneto-caloric effect, in these samples. Among them, the magnetic entropy change reaches a maximum value of 6.5 J/kg K at 260 K and 5 J/kg K at 293 K for $x = 0.00$ and 0.25 at the applied field of 13.5 kOe, respectively. The magnetic entropy of a manganite $La_{0.7}(Ca_{0.75}Sr_{0.25})_{0.3}MnO_3$ is comparable to materials considered a suitable candidate for the advanced magnetic refrigeration technology

(Table 1). The large magnetic entropy change produced by the abrupt reduction of magnetization is attributed to the strong coupling between spin and lattice in the magnetic ordering process. There is spin glass-like state occurring in the samples. Giant magneto-caloric effect has been observed in sample $La_{0.7}(Ca_{0.75}Sr_{0.25})_{0.3}MnO_3$ around room temperature at moderate low field variation. A large magneto-caloric effect was measured at a Curie temperature, opening a way for the investigation of materials for magnetic refrigerators. So the studied materials could be considered as suitable candidates for active magnetic refrigeration working in large temperature range and in more realistic field.

Acknowledgement

Rerefences

[1] A.M. Tishin, in: K.H.J. Buschow (Ed.), Hand Book of Magnetic Materials, vol. 12, Elsevier, Amsterdam, 1999 (Chapter 4).
[2] H.B. Callen, Thermodynamics, Wiley, New York, 1981 (Chapter 14).
[3] V.K. Pecharsky, K.A. Gschneidner, J. Magn. Magn. Mater. 200 (1999) 44.
[4] E. Bruck, M. Ilyn, A.M. Tislim, O. Tegus, J. Magn. Magn. Mater. 290–291 (2005) 8.
[5] X.X. Zhang, J. Tejada, Y. Xin, G.F. Sun, K.W. Wong, X. Bohigas, Appl. Phys. Lett. 69 (1996) 3566.
[6] H. Huang, Z.B. Guo, D.H. wang, Y.W. Du, J. Magn. Magn. Mater. 173 (1997) 302.
[7] X. Bohigas, J. Tejada, E. Del Barco, X.X. Zhang, M. Sales, Appl. Phys. Lett. 73 (1998) 390.
[8] A. Szewezyk, H. Szymczak, A. Wisniewski, K. Piotrowski, R. kartaszynski, B. Dabrowski, S. Kolesnik, z. Bukowski, Appl. Phys. Lett. 77 (2000) 1026.
[9] N.H. Luong, N. Chau, P.M. Huong, D.L. Minh, N.N. Chau, B.T. Cong, M. Kurisu, J. Magn. Magn. Mater. 242–245 (2002) 760.
[10] N. Chau, P.Q. Niem, H.N. Nhat, N.H. Luong, N.D. Tho, Physica B 327 (2003) 214.
[11] Md.A. Choudhury, S.A. Akhter, D.L. Minh, N.D. Tho, N. Chau, J. Magn. Magn. Mater. 272–276 (2004) 1295.
[12] M.H. Phan, N.D. Tho, N. Chau, S.C. Yu, M. Kurisu, J. Appl. Phys. 97 (2005) 103901.
[13] M.H. Phan, T.L. Phan, S.C. Yu, N.D. Tho, N. Chau, Phys. Stat. Sol. (b) 241 (2004) 1744.
[14] M.H. Phan, H.X. Peng, S.C. Yu, N.D. Tho, N. Chau, J. Magn. Magn. Mater. 290 (2005) 199.
[15] N. Chau, H.N. Nhat, N.H. Luong, D.L. Minh, N.D. Tho, N.N. Chau, Physica B 327 (2003) 270.
[16] N.H. Luong, D.T. Hanh, N. Chau, N.D. Tho, T.D. Hiep, J. Magn. Magn. Mater. 290 (2005) 690.
[17] N. Chau, D.H. Cuong, N.D. Tho, H.N. Nhat, N.H. Luong, B.T. Cong, J. Magn. Magn. Mater. 272 (2004) 1292.
[18] N. Chau, N.D. The, C.X. Huu, in: Proceedings of the Second International Workshop on Nanophysics and Nanotechnology, Hanoi, Vietnam, October 22–23, 2004, p. 51.
[19] Z.B. Guo, Y.W. Du, J.S. Zhu, H. Huang, W.P. Ding, D. Feng, Appl. Phys. Lett. 88 (1997) 1142.
[20] L.E. Hueso, P. Sande, D.R. Miguens, J. Rivas, F. Rivadulla, M.A. Lopez-Quintela, J. Appl. Phys. 91 (2002) 9943.
[21] Y. Sun, X. Xu, Y.H. Zhang, J. Magn. Magn. Mater. 219 (2000) 183.
[22] T.D. Hiep, N. Chau, N.D. Tho, N.H. Luong, in: Proceedings of the Ninth Vietnam Biennal Conference on Radio and Electronics (REV'04), Hanoi, Vietnam, November 26–27, 2004, p. 339.
[23] J. Mira, J. Rivas, L.E. Hueso, F. Rivadulla, M.A. Lopez-Quintela, J. Apply. Phys. 91 (2002) 8903.
[24] M. Foldeaki, R. Chahine, T.k. Bose, J. Appl. Phys 77 (1995) 3528.
[25] A. Arulraj, P.N. Santhoh, R.S. Gopalan, A. Guha, A.K. Raychaudhuri, N. Kumar, C.N.R. Rao, J. Phys. Condens. Matter 10 (1998) 8497.
[26] Z.H. Wang, T.H. Ji, Y.Q. Wang, X. Chen, R.W. Li, J.W. Cai, J.R. Sun, B.G. Shen, C.H. Yan, J. Appl. Phys. 87 (2000) 5582.
[27] S.Y. Dankov, A.M. Tishin, V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. B 57 (1998) 3478.