Determination of the magnetocaloric effect associated with martensitic transition in $Ni_{46}Cu_4Mn_{38}Sn_{12}$ and $Ni_{50}CoMn_{34}In_{15}$ Heusler alloys*

Li Zhe(李 哲), Jing Chao(敬 超)†, Zhang Hao-Lei(张浩雷), Cao Shi-Xun(曹世勋), and Zhang Jin-Cang(张金仓)

Department of Physics, Shanghai University, Shanghai 200444, *China*

(Received 31 July 2010; revised manuscript received 6 November 2010)

This paper presents a study of the inverse magnetocaloric effect (MCE) corresponding to martensitic transition using various experimental approaches for $Ni_{46}Cu_4Mn_{38}Sn_{12}$ and $Ni_{50}CoMn_{34}In_{15}$ Heusler alloy. Through heat capacity measurements, it is found that the "giant inverse MCE" upon martensitic transition evaluated by the Maxwell relation in these alloys are unphysical results. This is due to the coexistence of both martensitic and austenitic phases, as well as thermal hysteresis during martensitic transition. However, careful study indicates that the spurious results during martensitic transition can be removed using a Clausius–Clapeyron equation based on magnetization measurements.

Keywords: Heusler alloy, martensitic transition, magnetocaloric effect

PACS: 75.50.Cc, 81.30.Kf, 75.30.Sg **DOI:** 10.1088/1674-1056/20/4/047502

1. Introduction

Since the discovery of the giant magnetocaloric effect (MCE) in the $Ga_5Si_2Ge_2$ alloy near room temperature,[1] magnetocaloric materials have drawn worldwide attention due to their potential application for magnetic refrigeration. During the past decade, an intensive amount of work has concentrated on the study of MCE in other giant magnetocaloric materials, such as $MnFeP_{1-x}As_x$, $La(Fe_{1-x}Si_x)_{13}$ and $MnAs_{1-x}Sb$.[2,3] A common property among these materials is that they undergo a first-order magnetostructural phase transition (FOMT). As is well known, one of the important parameters for evaluating MCE is the isothermal entropy change ($\Delta S_{\rm T}$), which can usually be determined by two experimental methods, including the Maxwell relation method and the heat capacity method. The simplest and most used experimental method to determine $\Delta S_{\rm T}$ is from magnetization measurements, using a Maxwell relation with a numerical method[4]

$$\Delta S_{\rm T} = \int_0^H \left(\frac{\partial M(H,T)}{\partial T}\right) \approx \sum \frac{(M_{n+1}-M_n)_H}{T_{n+1}-T_n}\Delta H_n, \quad (1)$$

where M_{n+1} and M_n are the magnetization values measured in a field H, at temperatures of T_{n+1} and T_n, respectively. This method has proven to be very useful when dealing with magnetocaloric samples undergoing second-order magnetic transition. However, the determination of $\Delta S_{\rm T}$ with FOMT often results in overestimation due to the coexistence of two phases.

In recent years, a new type of ferromagnetic shape memory alloys have been found in Mn-rich Ni–Mn based Heusler alloys, which also undergo FOMT from a high-symmetry austenitic phase to a low-symmetry martensitic phase with an abrupt drop of magnetization in the cooling process.[5] Due to the large and rapid temperature variation in the magnetic interaction around martensitic transition, a giant inverse MCE has been observed in the narrow temperature range (i.e. a "sharp peak" has been customarily observed around transition point in their $\Delta S_{\rm T}$–T curves) for these alloys through a simple magnetization measurements (via Maxwell relation).[6–11] For magnetocaloric materials with FOMT, detailed investigations based on thermometric measurements have verified that the intrinsic nature of their MCE should be reflected by the flat plateau in the $\Delta S_{\rm T}$–T curves, whereas an extremely high spike followed by

*Project supported by the Science Foundation of Surface Physics Laboratory (National Key Laboratory) of Fudan University (Grant No. FDS2008-B01), the Graduate Innovation Foundation of Shanghai University (Grant Nos. SHUCX101065 and SHUCX102011) and the National Natural Science Foundation of China (Grant Nos. 50932003 and 10804068).

†Corresponding author. E-mail: cjing@staff.shu.edu.cn

© 2011 Chinese Physical Society and IOP Publishing Ltd

a flat plateau is a spurious signal.[3,12,13] Lately, the correct evaluation of $\Delta S_{\rm T}$ related to the MCE with martensitic transition in a Heusler alloys system has caused much discussion.[14−16] Thus, we believe that the evaluation method for inverse MCE in the vicinity of martensitic transition needs to be reconsidered for Heusler alloy systems.

In this paper, we shall study the inverse MCE during martensitic transition in $Ni_{46}Cu_4Mn_{38}Sn_{12}$ and $Ni_{50}CoMn_{34}In_{15}$ Heusler alloys. The values of $\Delta S_{\rm T}$ obtained from magnetization (via Maxwell relation) and heat capacity measurements are compared. We explain the origin of the spurious peak and provide a quantitative computation of its magnitude based on magnetization measurements.

2. Experiment

In experiment, polycrystalline $Ni_{46}Cu_4Mn_{38}Sn_{12}$ and $Ni_{50}CoMn_{34}In_{15}$ alloys with nominal composition were fabricated by a conventional arc-melting method. The weight losses of both samples after melting were found to be less than 0.5%. The obtained ingots were annealed in an evacuated quartz capsule for 24 hours at 1173 K and subsequently quenched in ice water. X-ray diffraction (XRD) determined that both samples had $L2_1$ ordered structures at room temperature. Isothermal magnetization curves and heat capacity data were acquired in the temperature range of 5 K–315 K at a magnetic field from 0 to 90 kOe (1 Oe = 79.5775 A/m) with a physical property measurement system (PPMS-9, Quantum Design Inc.).

3. Results and discussion

Figure 1 shows the temperature dependence of magnetization (M–T) curves for both samples on cooling and heating in a magnetic field of 0.5 kOe. For $Ni_{46}Cu_4Mn_{38}Sn_{12}$ sample, we can see two FOMTs during cooling and heating in the temperature range of 270 K–290 K with an obvious hysteresis, indicating that a direct martensitic transformation and a reverse martensitic transition occur [see Fig. 1(a)]. From Fig. 1(b), the M–T curve of $Ni_{50}CoMn_{34}In_{15}$ displays a similar behaviour. In addition, all of the characteristic temperatures, such as martensite start ($M_{\rm s}$), martensite finish ($M_{\rm f}$), austenite start ($A_{\rm s}$) and austenite finish ($A_{\rm f}$), appreciably decrease. Such behaviour is helpful for us to tune the FOMT in a Heusler alloys system, which is important for magnetic refrigeration field applications.

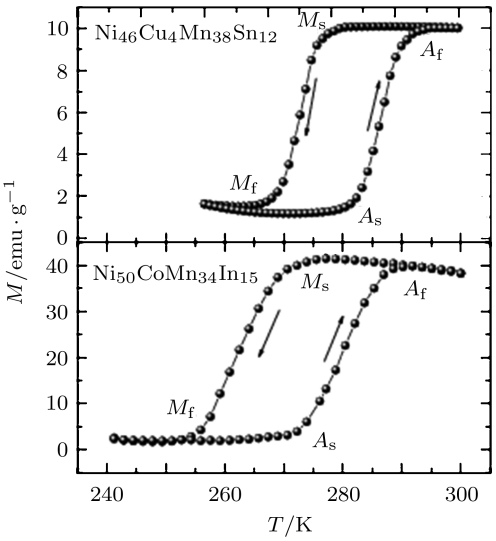


Fig. 1. Temperature dependence of magnetization measured at H = 0.5 kOe: (a) $Ni_{46}Cu_4Mn_{38}Sn_{12}$ and (b) $Ni_{50}CoMn_{34}In_{15}$.

We measured the isothermal magnetization curves of both samples upon their direct martensitic transition, shown in Figs. 2(a) and 2(c). The magnetizations of these alloys decrease with decreasing temperature, leading to a large difference in magnetization (ΔM) between the austenitic and martensitic phases. This implies that a considerable $\Delta S_{\rm T}$ can be expected in both samples. To check this, the inverse MCE of both samples were evaluated from these magnetization curves [See Figs. 2(a) and 2(c)] using Eq. (1) and the corresponding results are presented in Figs. 2(b) and 2(d). It is obvious that there are sharp peaks in the $\Delta S_{\rm T}$–T curves near $M_{\rm s}$, the maximum $\Delta S_{\rm T}$ achieves ∼67 J/kg · K and ∼50 J/kg · K for magnetic field change of 90 kOe in $Ni_{46}Cu_4Mn_{38}Sn_{12}$ and $Ni_{50}CoMn_{34}In_{15}$, respectively. These values are significantly larger than that in well-known magnetocaloric materials with FOMT (such as $Ga_5Si_2Ge_2$ etc.) under similar conditions,[1−3] and are said to have a "giant inverse MCE" like those reported for the Ni–Mn-based family of alloys.[6−11] Does this experimental method reflect the intrinsic nature of inverse MCE during martensitic transition? In order to answer this question, we selected $Ni_{46}Cu_4Mn_{38}Sn_{12}$ and studied it with heat capacity measurements. Figure 3 gives the heat capacity measurements of $Ni_{46}Cu_4Mn_{38}Sn_{12}$ at 0 and 90 kOe on heating mode. From the $C_{\rm p}$–T curves, we calculated the isothermal entropy change upon transition and plot the $\Delta S_{\rm T}$–T curves in the magnetic field change of 90 kOe, as shown in the inset of Fig. 3. The $\Delta S_{\rm T}$ curve calculated by magnetic measurements (via Eq. (1)) is very different from the $\Delta S_{\rm T}$–T curve obtained from heat capacity. It exhibits a flat plateau

and the maximum height is only ∼17 J/kg·K. We think that this phenomenon should accurately reflect the intrinsic nature of MCE for $Ni_{46}Cu_4Mn_{38}Sn_{12}$ with martensitic transition. In addition, the "sharp peaks" in the ΔS_T–T curves deduced by magnetic measurements (via Eq. (1)) represent unrealistic behaviour and are due to incorrect experimental method. Such method does not take into account the coexistence of both martensitic and austenitic phases as well as thermal hysteresis during martensitic transition. Obviously, the ΔS_T calculated by Eq. (1) from the magnetic measurements above is proportional to the area between two adjacent magnetization curves. Due to the effect of thermal hysteresis, a large part of area between the two adjacent magnetization curves [marked by hatched part in Figs. 2(a) and 2(c)] should mainly consist of the activities of the magnetic moments in the remaining volume of austenitic phase.

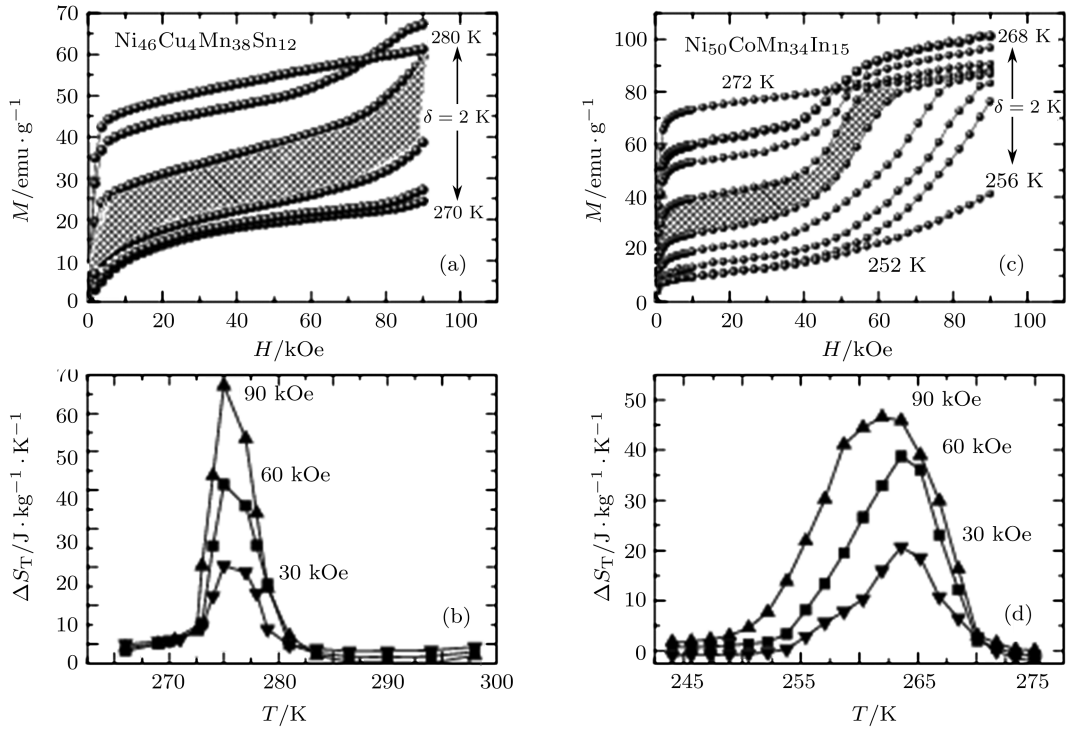


Fig. 2. (a) Isothermal magnetization curves of $Ni_{46}Cu_4Mn_{38}Sn_{12}$ measured around direct martensitic transition. (b) Temperature dependence of isothermal entropy change under various magnetic field changes. (c) and (d) The corresponding results for $Ni_{50}CoMn_{34}In_{15}$.

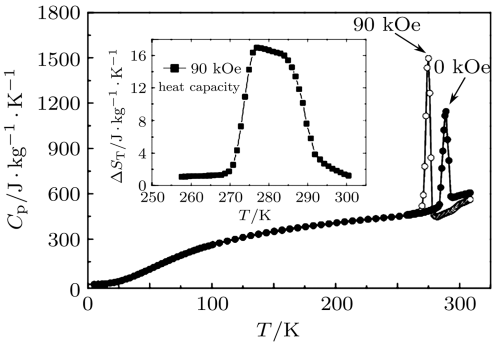


Fig. 3. Heat capacity measured under magnetic fields of 0 and 90 kOe on heating mode for $Ni_{46}Cu_4Mn_{38}Sn_{12}$. The inset is an isothermal entropy curve deduced by heat capacity results.

In reality, the remaining austenitic phase does not contribute to the inverse MCE. As a result, using Eq. (1), we integrated the normalized area in the calculation of ΔS_T, resulting in a "giant inverse MCE" of $Ni_{46}Cu_4Mn_{38}Sn_{12}$ is a nonphysical result.

To avoid the effect of thermal hysteresis, we then measured the isothermal magnetization curves during reverse martensitic transition in $Ni_{46}Cu_4Mn_{38}Sn_{12}$, as shown in Fig. 4(a). These curves exhibit markedly field-induced reverse martensitic transition (FIRMT), i.e., metamagnetic transition, starting at about 272 K and being complete at about 292 K. The metamagnetic transition is an important characteristic of magnetocaloric materials with FOMT.[12,13] From these results, the ΔS_T–T curves are plotted at various magnetic fields using Eq. (1), as shown in Fig. 4(b). With an increasing magnetic field, the peak of ΔS_T gradually expands to lower temperatures and then becomes plateau-like with a maximum height of ∼30 J/kg·K.

This value is cosiderablely lower than those determined from direct martensitic transition under the same condition, testifying that the former experimental method is not reliable.

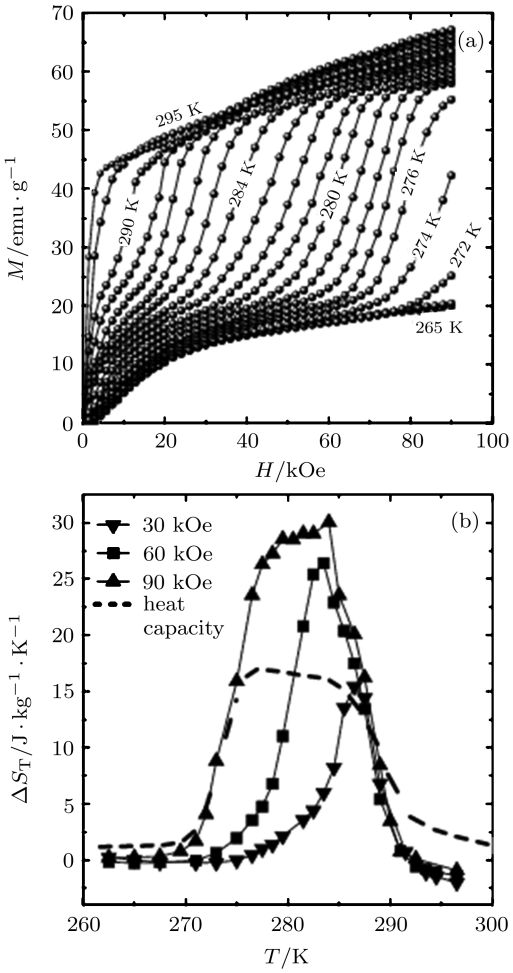


Fig. 4. (a) The isothermal magnetization curves measured around the reverse martensitic transition for $Ni_{46}Cu_4Mn_{38}Sn_{12}$. (b) Isothermal entropy change calculated from these magnetization curves based on Maxwell relation. The dashed line shows the isothermal entropy change obtained from heat capacity measurements under 0–90 kOe field change.

However, figure 4(b) also shows a large amount of discrepancy between the magnetic and heat capacity measurements, which implies that the ΔS_T in $Ni_{46}Cu_4Mn_{38}Sn_{12}$ predicted by the Maxwell relation in metamagnetic transition region is so far unsuccessful. For magnetocaloric materials with FOMT, many experimental studies have been stated that the ΔS_T determined by the Maxwell relation is creditable when materials are in a pure magnetic state under a saturated applied field.[3,12−14] For our sample, however, excess Mn atoms occupying the Sn sites are coupled antiferromagnetically to the surrounding Mn atoms on regular Mn sites of the austenitic phase, which is then distinctly strengthened due to martensitic transition, highlighting the fact that a magnetically inhomogeneous state coexists in ferro- and antiferromagnetic regions around the transition point.[17,18] Furthermore, if we depart from thermodynamics relations of isothermal entropy change, we can find that the $\partial M/\partial T$ cannot be regarded as being independent owing to the fact that FIRMT in Heusler alloys system is mostly accompanied by a change of macroscopic volume. In view of these points, the Maxwell relation method based on magnetic measurements is difficult to equitably estimate inverse MCE during martensitic transition for Heusler alloys system.

For a Heusler alloys system, the Clausius–Clapeyron (C–C) equation offers a good way to calculate the ΔS_T around its martensitic transition. The ΔS_T determined in this way is related to the ΔM induced by the field at a given temperature, i.e., ΔM corresponds uniquely to the transformation of a martensitic to austenitic phase. This equation is written as

$$|\Delta S_T| = \left|\Delta M \frac{dH_C}{dT}\right|. \quad (2)$$

The ΔM of $Ni_{46}Cu_4Mn_{38}Sn_{12}$ is exactly identified by Arrot-plot[19] in order to avoid some errors, as shown in Fig. 5(a), while the dH_C/dT obtained from the linear fitting of the average H_C versus T is about 5.3 kOe/K [see Fig. 5(b)]. It is worth while noting that equation (2) is equivalent to Eq. (1) for an approximately ideal metamagnetic transition region. The ΔS_T–T curves for $Ni_{46}Cu_4Mn_{38}Sn_{12}$ under various magnetic fields replotted by Eq. (2) are shown in Fig. 5(c). It can be clearly seen that the ΔS_T–T curve is satisfactorily in accordance with the heat capacity measurements for a magnetic field change of 90 kOe, proving that the others plotted in this way are also equitable. For a magnetic field change of 60 kOe, the temperature span of ΔS_T is distinctly reduced, this is accompanied by a the flat plateau of ΔS_T moving to high temperature, whereas the height of ΔS_T remains almost unchanged. It indicates that an large enough magnetic field can increase the temperature span of ΔS_T, but the effect on value of ΔS_T is minimal due to the saturation of ΔM. With a further decrease of the magnetic field change (30 kOe), the ΔS_T suddenly attains a sharp peak value but then evidently decreases. Such a behaviour can be interpreted by the fact that the martensitic transition of $Ni_{46}Cu_4Mn_{38}Sn_{12}$ affected by a low magnetic field is so weak that FIRMT is not integrated.

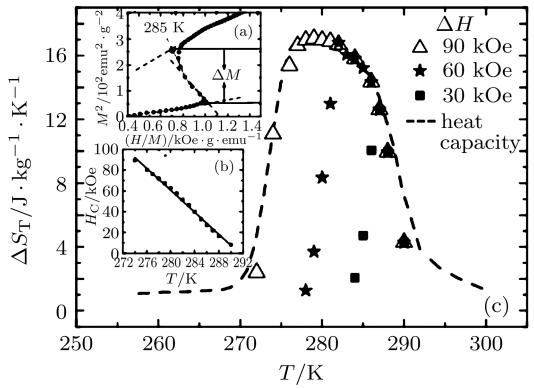


Fig. 5. (a) The ΔM identified by Arrot-plot. (b) The $\mathrm{d}H_\mathrm{C}/\mathrm{d}T$ obtained from linear fitting of the average H_C versus T. (c) Isothermal entropy change calculated from metamagnetic isothermal curves based on Clausius–Clapeyron for $Ni_{46}Cu_4Mn_{38}Sn_{12}$, dash line shows the isothermal entropy change obtained from heat capacity measurements under 0–90 kOe field change.

Thereafter, we also reconsider the inverse MCE for $Ni_{50}CoMn_{34}In_{15}$ with martensitic transition using the same approach. The corresponding results are shown in Fig. 6. It can clearly be seen that the maximum of ΔS_T is only about one half of that obtained from the Maxwell relation under the same magnetic field change. Moreover, the ΔS_T–T curves of $Ni_{50}CoMn_{34}In_{15}$ show a flat plateau like the one for $Ni_{46}Cu_4Mn_{38}Sn_{12}$, but the height of plateau is larger than that of $Ni_{46}Cu_4Mn_{38}Sn_{12}$ owing to the enhancement of ΔM in $Ni_{50}CoMn_{34}In_{15}$. This further confirms that the C–C equation based on magnetization measurements is a good method for estimating the inverse MCE upon martensitic transition for a Heusler alloys system.

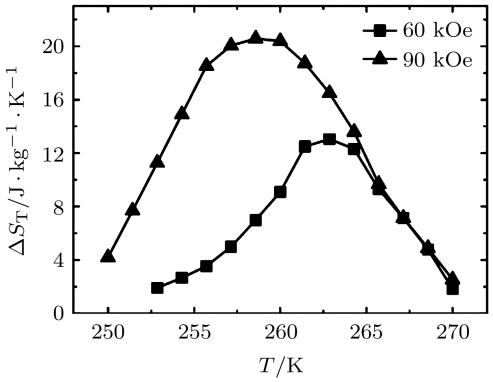


Fig. 6. Isothermal entropy change calculated from metamagnetic isothermal curves based on C–C for $Ni_{50}CoMn_{34}In_{15}$.

4. Conclusions

In summary, our results indicate that the inverse MCE in the case of martensitic transition for the Heusler alloys system is easily misjudged when employing the Maxwell relation due to thermal hysteresis and a mixed phase at the martensitic state, and a more credible method is the C–C equation. This discussion can help with equitably dealing with the inverse MCE associated with martensitic transition in a Ni–Mn-based Heusler alloys system.

References

[1] Pecharsky V K and Gschneidner K A Jr 1997 *Phys. Rev. Lett.* **78** 4494

[2] Tishin A M and Spichkin Y 2003 *The Magnetocaloric Effect and Its Applications* (Bristol: IOP Publishing Ltd) p. 4

[3] Shen B G, Sun J R, Hu F X, Zhang H W and Cheng Z H 2009 *Adv. Mater.* **21** 4545

[4] Pecharsky V K and Gschneidner K A Jr 1999 *J. Appl. Phys.* **86** 6315

[5] Sutou Y, Imano Y, Koeda N, Omori T, Kainuma R, Ishida K and Oikawa K 2004 *Appl. Phys. Lett.* **85** 4358

[6] Krenke T, Duman E, Acet M, Wassermann E F, Moya X, Mañosa L and Planes A 2005 *Nature Mater.* **4** 450

[7] Han Z D, Wang D H, Zhang C L, Tang S L, Gu B X and Du Y W 2006 *Appl. Phys. Lett.* **89** 182507

[8] Nayak A K, Suresh K G and Nigam A K 2009 *J. Phys.* D: *Appl. Phys.* **42** 035009

[9] Jing C, Li Z, Chen J P, Lu Y M, Cao S X and Zhang J C 2008 *Acta Phys. Sin.* **57** 3780 (in Chinese)

[10] Jing C, Chen J P, Li Z, Cao S X and Zhang J C 2008 *Acta Phys. Sin.* **57** 4450 (in Chinese)

[11] Jing C, Li Z, Zhang H L, Chen J P, Qiao Y F, Cao S X and Zhang J C 2009 *Euro. Phys. J.* B **67** 193

[12] Tocado L, Palacios E and Burriel R 2009 *J. Appl. Phys.* **105** 093918

[13] Balli M, Fruchart D, Gignoux D and Zach R 2009 *Appl. Phys. Lett.* **95** 072509

[14] Zou J D, Shen B G, Gao B, Shen J and Sun J R 2009 *Adv. Mater.* **21** 693

[15] Mañosa L, Planes A and Moya X 2009 *Adv. Mater.* **21** 3725

[16] Zou J D, Shen B G, Gao B, Shen J and Sun J R 2009 *Adv. Mater.* **21** 3727

[17] Krenke T, Acet M, Wassermann E F, Moya X, Mañosa L and Planes A 2005 *Phys. Rev.* B **72** 014412

[18] Li Z, Jing C, Chen J P, Yuan S J, Cao S X and Zhang J C 2007 *Appl. Phys. Lett.* **91** 112505

[19] Arrot A 1957 *Phys. Rev.* **108** 1394