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Pressure effects in the giant magnetocaloric compounds $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$

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Abstract

We report a study of the effect of hydrostatic pressure up to 9 kbar on selected compounds of the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ series ($x = 0.8, 0.45, 0.1$) by means of ac magnetic susceptibility, compressibility, and linear thermal expansion measurements. The pressure-induced increase of the transition temperatures at the second-order boundaries of the phase diagram is rather moderate: $dT_C/dP \cong +0.3 \text{ K kbar}^{-1}$ ($x = 0.8$) and $dT_N/dP \cong +0.7 \text{ K kbar}^{-1}$ ($x = 0.1$). This effect is stronger in the $0 < x \leq 0.5$ range, where $dT_C/dP \cong +3 \text{ K kbar}^{-1}$ ($x = 0.45, 0.1$), indicating that the ferromagnetic ordering can be simultaneously driven through a pressure-induced structural transformation. The values of $d \ln T_C / d \ln V$ calculated with the use of the measured value of compressibility ($\kappa \cong 1.8 \text{ Mbar}^{-1}$) are significantly lower than those estimated from the concentration dependence of the lattice cell volume, thus demonstrating that the dependence of the transition temperatures upon changing the Si/Ge ratio across the series cannot be explained by a pure volume effect.

1. Introduction

$\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ is considered a unique class of materials where many interesting properties and intriguing behaviours have been recently discovered [1]. We can highlight the unprecedented giant magnetocaloric effect [2], strong magnetoelastic effects [3, 4], and giant magnetoresistance [5, 6]. This phenomenology has been associated with the intrinsically layered crystallographic structure combined with a magnetic–martensitic first-order phase

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transformation [7]. The coupled magnetic–crystallographic transition can be induced reversibly by changing external parameters such as temperature, external magnetic field, and hydrostatic pressure [1, 4]. Therefore, these alloys are attractive because of their potential applications in magnetic refrigeration and/or as magnetostrictive/magnetoresistive transducers.

The phase relationships, crystallography, and magnetic phase diagram were initially proposed in [8] and recently revised [9]. A total of three extended solid solution regions were confirmed: the Si-rich solid solution, $0.575 \leq x \leq 1$, has the orthorhombic Gd_5Si_4 -type structure (O(I)) belonging to the $Pnma$ space group; the intermediate phase $0.4 < x \leq 0.503$ has a room-temperature monoclinic (M) structure, space group $P112_1/a$; and the Ge-rich region, $0 \leq x \leq 0.3$ crystallizes in the Gd_5Ge_4 -type structure (O(II)), also in the orthorhombic $Pnma$ space group. All three structures are composed of identical two-dimensional (2D) subnanometre-thick layers (slabs) interconnected via partially covalent interslab X–X bonds (X = Si, Ge). In the O(I) structure, all the slabs are interconnected by X–X bonds; half of these bonds are broken in the M structure and none remain in the O(II) structure. The magnetic–crystallographic transition involves breaking and reforming specific covalent X–X bonds [7] and the low-temperature ground state for all compositions $0 < x \leq 1$ is always ferromagnetic (FM) with all the slabs being interconnected, i.e. with the O(I) structure. The M structure is always paramagnetic (PM) whereas O(II) can support either PM or antiferromagnetism (AFM) [4, 9]. The magnetic ground state of the parent Gd_5Ge_4 alloy is AFM with a Néel temperature of ~ 130 K and presents a very complex magnetic field–temperature (H – T) phase diagram, and an interesting magnetoelastic behaviour [10, 11].

Despite the strong coupling between crystallographic and magnetic degrees of freedom in these systems resulting in strong volume effects [3, 4, 11], no systematic study of the effect of hydrostatic pressure has been carried out. Preliminary results were published in [3] on $x = 0.45$. In this paper we report a complete investigation of the pressure effects in the giant magnetocaloric compounds $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ ($x = 0.8, 0.45, 0.1$) by means of ac susceptibility, compressibility, and linear thermal expansion under a hydrostatic pressure of up to 9 kbar. Our study demonstrates that the dependence of the transition temperatures upon changing the Si/Ge ratio across the series cannot be explained by a pure volume effect.

2. Experiment

The alloys with nominal composition $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ ($x = 0.8, 0.45, 0.1$) were synthesized by arc melting of 99.9 wt% pure Gd and 99.9999 wt% pure Si and Ge under a high-purity argon atmosphere. Weight losses during melting were negligible and, therefore, the initial compositions were assumed unchanged. The quality of all of the samples used in the present study was checked by means of room-temperature x-ray diffraction and scanning electron microscopy with electron-beam microprobe analysis. These studies confirmed the existence of a monoclinic 5:4 majority phase in the $x = 0.45$ specimen, and a Gd_5Ge_4 -type orthorhombic phase in the $x = 0.1$ alloy. The impurity phases ($\approx 7\%$) have been identified as being Gd_5Si_4 -type orthorhombic with composition $\text{Gd}_5(\text{Si}_{0.525}\text{Ge}_{0.475})_4$ ($x = 0.45$), and hexagonal $\text{Gd}_5(\text{Si}, \text{Ge})_3$ ($x = 0.1$); the $x = 0.8$ sample is single phase within the experimental resolution. The $x = 0.45$ and 0.1 samples were the same as used in earlier studies [3–5].

The pressure experiments were carried out under hydrostatic pressure up to 9 kbar in a standard Cu–Be piston–cylinder cell. A mixture of mineral oils was used as the pressure transmitting medium and the pressure values at different temperatures were determined using a manganin pressure sensor. The ac magnetic susceptibility, χ_{ac} , at ambient and high pressures was measured by the usual transformer method. Linear thermal expansion (LTE) and compressibility measurements under pressure were performed using the strain-gauge technique.

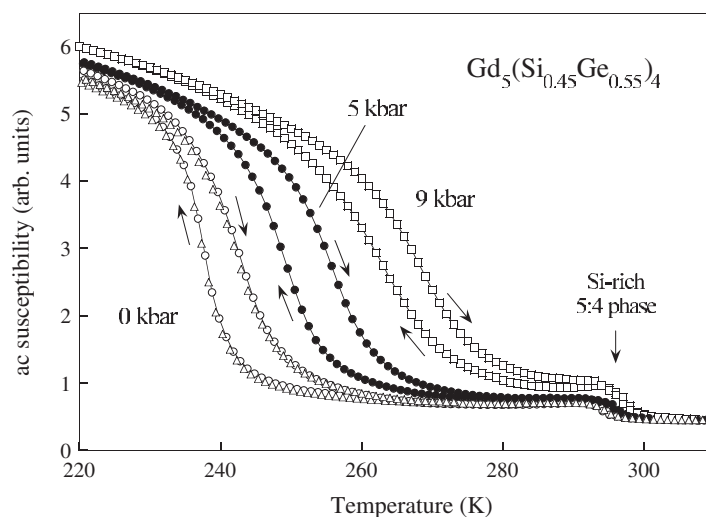


Figure 1. ac magnetic susceptibility of the $x = 0.45$ alloy as a function of temperature at ambient (\circ) and under selected hydrostatic pressures of 5 (\bullet) and 9 kbar (\square) (values at room temperature). A signal from a Si-rich 5:4 minor impurity with composition $x = 0.525$ [3] is distinctly seen and marked in the figure. After the pressure study, a zero-pressure run was repeated (Δ). Solid arrows indicate the direction of temperature change.

3. Results and discussion

The $x = 0.45$ alloy undergoes a first-order M (PM) \rightarrow O(I) (FM) crystallographic–magnetic transition on cooling at $T_C \approx 240$ K. In figure 1 we display the χ_{ac} measurements as a function of temperature at ambient and under selected hydrostatic pressures of 5 and 9 kbar (values at room temperature). The values of all the transition temperatures have been taken at the maximum $d\chi_{ac}/dT$ values. As a general trend, the transition temperature increases with pressure, the hysteresis of ~ 6 K remaining unchanged. The increase of T_C with pressure is linear in the measured pressure range, see figure 2, and a value of $dT_C/dP = +3.00(5)$ K kbar $^{-1}$ has been derived. This value is 17% smaller than the one determined previously from LTE measurements [3]. A possible reason may be the fact that the determination of T_C is influenced by the shape of the curve being monitored and its change under pressure (the transition region gets smoother under pressure), thus introducing some uncertainty in the dT_C/dP value. Therefore, the similar dT_C/dP values measured by means of magnetic measurements (this work, figure 1) and from LTE experiments [3] are consistent with the fact that the magnetic and crystallographic transformations are coupled and remain coupled under pressure, confirming the important role of the interatomic distances in driving the magnetostructural transformation.

In addition, the presence in the χ_{ac} measurements of a distinct signal from a Si-rich 5:4 impurity, see figure 1, with composition $x = 0.525$ [3], has allowed us to determine the dependence of T_C versus pressure at the second-order Curie transition in the O(I) structure. A value of $dT_C/dP = +0.30(3)$ K kbar $^{-1}$ is obtained, one order of magnitude smaller than that of the main phase; see figure 2. We have checked this value by measuring χ_{ac} at different pressures for a single-phase sample with composition $\text{Gd}_5(\text{Si}_{0.8}\text{Ge}_{0.2})_4$, the results being in perfect agreement. Our results are also in very good agreement with the 0.29 K kbar $^{-1}$ value reported for the parent Gd_5Si_4 compound [12]. It is also important to point out that the relative amounts of monoclinic and orthorhombic phases within the $x = 0.45$ sample remain unchanged with pressure. To demonstrate this point we remeasured the ambient pressure curve

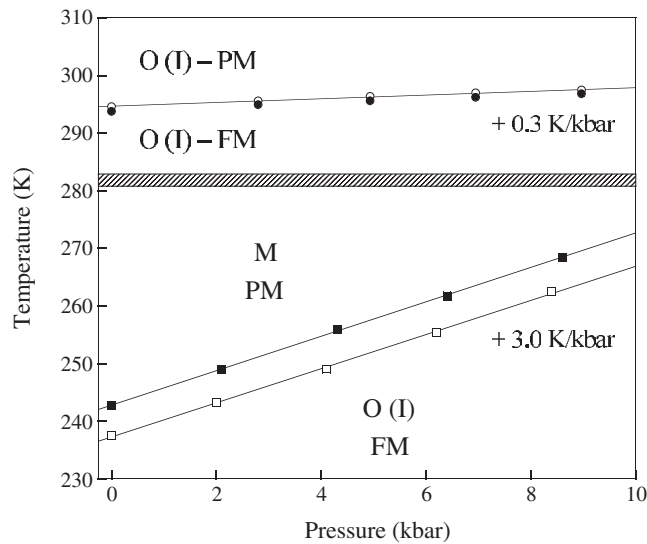


Figure 2. The temperature–pressure (T – P) phase diagram as obtained from ac magnetic susceptibility under pressure in the $x = 0.45$ sample. The horizontal hashed line separates data for two distinct phases having different room-temperature magnetic and crystallographic structures; see the introduction and [8, 9]: the upper set of data (circles) were obtained from the Si-rich 5:4 impurity (see figure 1) and the lower set were obtained from the transition associated with the main 5:4 phase as shown in figure 1. Error bars are within the symbol size used. The lines are linear fits and the values of the dT_C/dP slope obtained are indicated.

after all of the pressure study. The data obtained were, within the experimental error, identical to those from the zero-pressure run performed on the ‘virgin’ sample; see figure 1.

The $x = 0.1$ Ge-rich alloy undergoes on cooling a second-order PM \rightarrow AFM magnetic transition with no change in the O(II) structure at $T_N \cong 130$ K, and then a first-order O(II) (AFM) \rightarrow O(I) (FM) crystallographic–magnetic transformation at $T_C \cong 80$ K [4]. In figure 3 we display χ_{ac} in the vicinity of T_N at different pressures ranging from 0 to 9 kbar (values at room temperature). The dependences of the T_N values with pressure are plotted in the inset of figure 3 and a value of $dT_N/dP = +0.69(5)$ K kbar $^{-1}$ has been obtained. The shift of the O(II) (AFM) \rightarrow O(I) (FM) transition with pressure is identical to that of the M (PM) \rightarrow O(I) (FM) one, i.e. $\cong 3$ K kbar $^{-1}$, and thus independent of the large difference in the T_C values and of the different magnetic phases involved. We can explain this result by taking into account the Clausius–Clapeyron relation at a first-order transition in the form $dT/dP = \Delta V/\Delta S$, relating the slope in the P – T phase diagram to the change in volume ΔV and entropy ΔS involved in the transition. If we consider the ΔV either from x-ray diffraction (XRD) as a function of temperature [3, 4] or estimated from the unit cell volume versus composition [9], and values of ΔS from [13], we do get within the experimental uncertainty similar values for the two alloys (both ΔV and ΔS are higher for $x = 0.1$, but $\Delta V/\Delta S$ remains constant) and in good agreement with the experimental dT_C/dP value.

In order to evaluate the dependence of the magnetic interactions as a function of the unit cell volume, compressibility measurements were carried out for $x = 0.45$ and 0.1 at room temperature. For $x = 0.45$ the relative volume is linear over the pressure range investigated yielding a value of $\kappa = -(1/V)dV/dP = 1.82(1)$ Mbar $^{-1}$; see figure 4. The change of length versus pressure for $x = 0.1$ seems to be nonlinear up to 9.5 kbar. The compressibility ranges from 1.58 to 2.40 Mbar $^{-1}$, with a mean value of 1.9 Mbar $^{-1}$, very close to that for

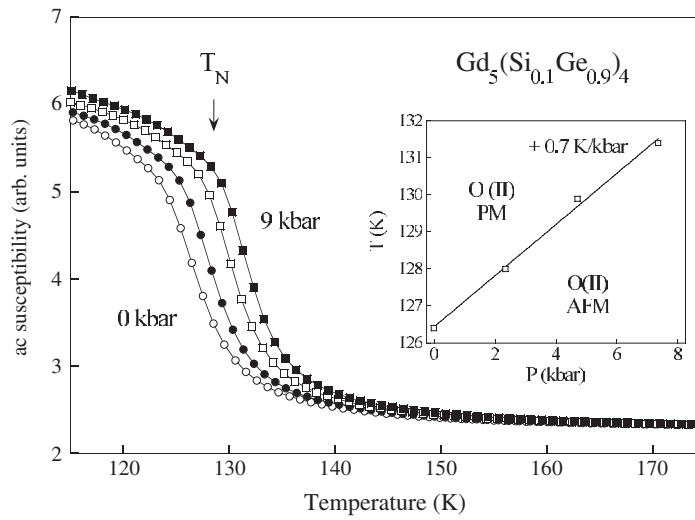


Figure 3. The ac magnetic susceptibility of the $x = 0.1$ alloy in the vicinity of the Néel transition under hydrostatic pressure values of 0 (\circ), 4 (\bullet), 7 (\square), and 9 (\blacksquare) kbar (values at room temperature). The T - P phase diagram and the value of the dT_N/dP slope are displayed in the inset.

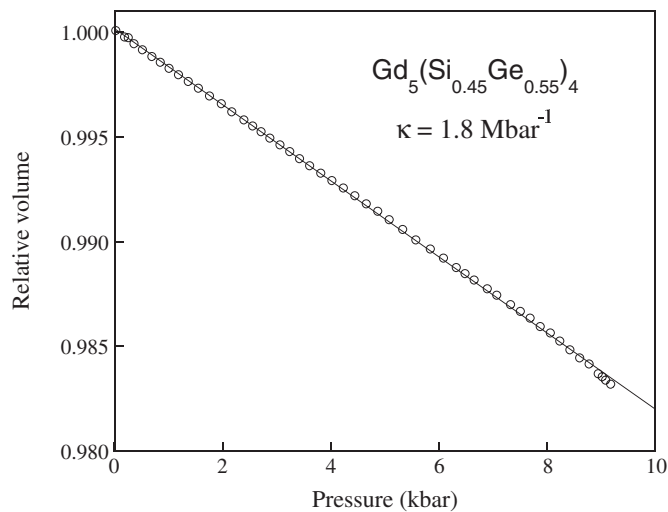


Figure 4. Relative volume for $x = 0.45$ as a function of pressure at room temperature. The compressibility value $\kappa = -(1/V) dV/dP$ has been indicated.

$x = 0.45$. At this point it is not clear whether this difference is extrinsic (inhomogeneities, cracks in sample, etc) or intrinsic, due to texture effects. As far as we know, no previous compressibility data have been reported for any of the $\text{R}_5(\text{SiGe})_4$ alloys, and, therefore, our results may be of importance e.g. for reinterpreting the data on a $\text{Gd}_5(\text{Si}_{0.43}\text{Ge}_{0.57})_4$ single crystal where a smaller value of 0.3 Mbar^{-1} was used [14].

A striking behaviour has been found in the LTE measurements for $x = 0.1$; see figure 5. As expected from the magnetic measurements, T_C shifts to higher temperatures at a rate of $\sim 3 \text{ K kbar}^{-1}$. However, the jump in the LTE at T_C changes magnitude and sign, from

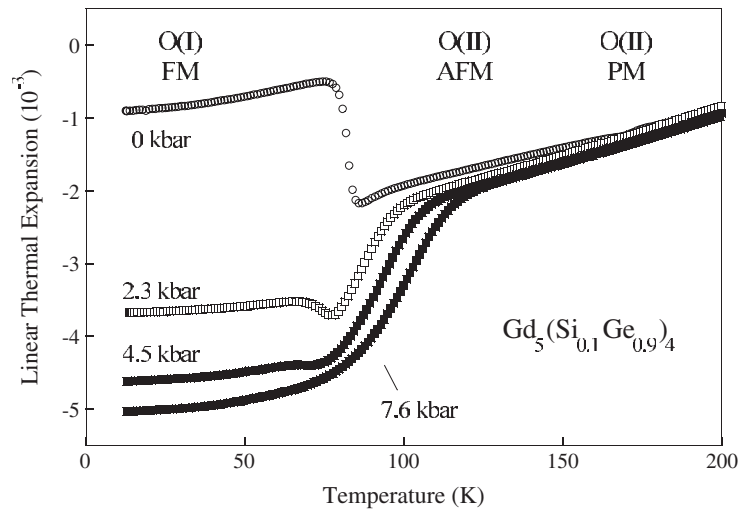


Figure 5. Linear thermal expansion (LTE) experiments for $x = 0.1$ at several selected applied hydrostatic pressures (values at the transition temperature, i.e. LTE jump).

$\Delta l/l \sim +0.16\%$ at 0 kbar to $\Delta l/l \sim -0.25\%$ at 9 kbar, the transition also getting smoother under pressure and the hysteresis gradually disappearing. These results are fully reproducible. Taking into account the XRD data [4] and thermal expansion measurements performed on single-crystalline $\text{Gd}_5\text{Si}_{2.09}\text{Ge}_{1.91}$ [14], a decrease in volume of $\sim 0.5\%$ should be observed when cooling through the transition from the AFM to the FM state. Due to the highly anisotropic behaviour of the lattice at this transition with a remarkable decrease of the a -parameter and slight increase of b - and c -parameters, such behaviour would only be observed for a non-textured polycrystalline sample. Consequently, the increase in length observed at ambient pressure indicates a remarkable texture, our LTE measurements most probably being performed on a surface close to the bc plane [4]. In order to explain the observed behaviour in our LTE measurements, we propose that the application of high pressure has a tendency to suppress the anisotropic behaviour of the lattice. Within this scenario, the temperature behaviours of all lattice parameters under sufficiently high pressures should be similar and a decrease of all lattice parameters at the transition on cooling should be observed. The gradual change of the anomaly and reproducibility of the observed behaviour during the different pressure runs supports this explanation. dc magnetization measurements (not shown here) also confirmed that the transition gets smoother with pressure although hysteresis persists, thus pointing to a more complex physical mechanism underlying the observed behaviour. In fact, the highest-pressure results for the $x = 0.1$ sample strikingly resemble those found for the parent Gd_5Ge_4 alloy where no spontaneous long-range ferromagnetism sets in at any temperature [15]. We might speculate that a complex nucleation process of the FM phase within the AFM phase is taking place with pressure instead of or overlapped with a simple shift of T_C with pressure. Magnetization and thermal expansion measurements under pressure on a single crystal and/or XRD under pressure would supply direct proof of the proposed explanation for our LTE results.

The magnetic behaviour of the $\text{R}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds can be understood qualitatively in terms of competition between intralayer (within the 2D slabs, conventional indirect 4f–4f RKKY) and interlayer exchange coupling (between slabs, direct Gd–Si/Ge–Gd superexchange propagated via the X–X bonds) [1, 16]. Furthermore, the occurrence of two distinct types of crystal structure in the PM phase (M and O(I) polymorphs) in the same alloy with $x \cong 0.5$ [17]

Table 1. The magnetic Grüneisen parameter $d \ln T_{C,N}/d \ln V$ derived from the values of the compressibility and $dT_{C,N}/dP$ determined in this work (Γ) and estimated from room-temperature structural data and the T - x phase diagram [9] (Γ^*).

x	Γ	Γ^*	Γ^*/Γ
0.8	-0.5	-7	14
0.45	-7	-87	12.4
0.1 (T_C)	-20	-167	8.4
0.1 (T_N)	-3	-14	4.7

has clearly demonstrated the paramount role of the interslab coupling in the magnetism of $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$. First-principles electronic structure calculations have helped to provide a better understanding: not only is the precise Si concentration, x , relevant, but so also is the specific ordering of Si and Ge atoms in the different crystallographic sites [18, 19]. From a different approach, the effect of hydrostatic pressure is that of changing the volume of the cell, thus enabling us to extract information on the dependence of the magnetic interactions with volume. From our experimental compressibility and $dT_{C,N}/dP$ values we can derive the magnetic Grüneisen parameter $\Gamma = d \ln T_{C,N}/d \ln V$ and compare with that estimated from room-temperature structural data and the T - x phase diagram [9], Γ^* . It is clear, see table 1, that the Γ values are significantly lower than the values of Γ^* . This indicates that the dependence of the transition temperatures upon changing the Si/Ge ratio across the series cannot be explained by a pure volume effect, and that significant changes both in the crystallographic bonding and electronic structure are taking place. Applying an external hydrostatic pressure reduces the X-X distance, thus favouring the interlayer interactions, and consequently increasing positively all transition temperatures. The effect is more pronounced at the $M \leftrightarrow O(\text{I})$ or $O(\text{II}) \leftrightarrow O(\text{I})$ transitions since breaking/reforming covalent X-X bonds takes place upon application of pressure.

4. Conclusions

In summary, we have found a positive increase of all transition temperatures in the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ giant magnetocaloric materials. In the case of second-order magnetic transitions with no change in the crystallographic structure, i.e. at the $\text{PM} \rightarrow \text{FM}$ one with $O(\text{I})$ structure, or the $\text{PM} \rightarrow \text{AFM}$ one with $O(\text{II})$ structure, a rather moderate effect has been found: $dT_C/dP \cong +0.3 \text{ K kbar}^{-1}$ ($x = 0.8$) and $dT_N/dP \cong +0.7 \text{ K kbar}^{-1}$ ($x = 0.1$). In contrast, a shift of $dT_C/dP \cong +3 \text{ K kbar}^{-1}$ has been obtained at the first-order magnetic-crystallographic phase boundary, i.e. either at the $M (\text{PM}) \rightarrow O(\text{I}) (\text{FM})$ or at the $O(\text{II}) (\text{AFM}) \rightarrow O(\text{I}) (\text{FM})$ transformation in $x = 0.45$ and 0.1 , respectively. This result can be explained by taking into account the Clausius-Clapeyron relation, $dT/dP = \Delta V/\Delta S$. We propose that breaking/reforming of covalent interlayer X-X bonds is taking place upon application of hydrostatic pressure. The values of $d \ln T_C/d \ln V$ calculated from our experimental study are significantly lower than those estimated from the concentration dependence of the lattice cell volume. This demonstrates the importance of the changes in the electronic structure versus changes in the unit cell volume upon changing the Si/Ge ratio in the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ series.

Acknowledgments

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References

- [1] Pecharsky V K and Gschneidner K A Jr 2001 *Adv. Mater.* **13** 683
- [2] Pecharsky V K and Gschneidner K A Jr 1997 *Phys. Rev. Lett.* **78** 4494
Pecharsky V K and Gschneidner K A Jr 1997 *Appl. Phys. Lett.* **70** 3299
Pecharsky V K and Gschneidner K A Jr 1997 *J. Magn. Magn. Mater.* **167** L179
- [3] Morellon L, Algarabel P A, Ibarra M R, Blasco J, García-Landa B, Arnold Z and Albertini F 1998 *Phys. Rev. B* **58** R14721
- [4] Morellon L, Blasco J, Algarabel P A and Ibarra M R 2000 *Phys. Rev. B* **62** 1022
- [5] Morellon L, Stankiewicz J, García-Landa B, Algarabel P A and Ibarra M R 1998 *Appl. Phys. Lett.* **73** 3462
Morellon L, Algarabel P A, Magen C and Ibarra M R 2001 *J. Magn. Magn. Mater.* **237** 119
- [6] Levin E M, Pecharsky V K and Gschneidner K A Jr 1999 *Phys. Rev. B* **60** 7993
- [7] Choe W, Pecharsky V K, Pecharsky A O, Gschneidner K A Jr, Young V G Jr and Miller G J 2000 *Phys. Rev. Lett.* **84** 4617
- [8] Pecharsky V K and Gschneidner K A Jr 1997 *J. Alloys Compounds* **260** 98
- [9] Pecharsky A O, Gschneidner K A Jr, Pecharsky V K and Schindler C E 2002 *J. Alloys Compounds* **338** 126
- [10] Levin E M, Gschneidner K A Jr and Pecharsky V K 2001 *Phys. Rev. B* **65** 214427
Levin E M, Pecharsky V K, Gschneidner K A Jr and Miller G J 2001 *Phys. Rev. B* **64** 235103
- [11] Magen C, Morellon L, Algarabel P A, Marquina C and Ibarra M R 2003 *J. Phys.: Condens. Matter* **15** 2389
- [12] Parviainen S 1980 *Phys. Status Solidi a* **60** K13
- [13] Casanova F, Battle X, Labarta A, Marcos J, Mañosa L and Planes A 2002 *Phys. Rev. B* **66** 212402
- [14] Nazih M, de Visser A, Zhang L, Tegus O and Brück E 2003 *Solid State Commun.* **126** 255
- [15] Magen C, Arnold Z, Morellon L, Skorokhod Y, Algarabel P A, Ibarra M R and Kamarad J 2003 *Phys. Rev. Lett.* **91** 207202
- [16] Levin E M, Pecharsky V K and Gschneidner K A Jr 2000 *Phys. Rev. B* **62** R14625
- [17] Pecharsky V K, Pecharsky A O and Gschneidner K A Jr 2002 *J. Alloys Compounds* **344** 362
- [18] Pecharsky V K, Samolyuk G D, Antropov V P, Pecharsky A O and Gschneidner K A Jr 2003 *J. Solid State Chem.* **171** 57
- [19] Samolyuk G D and Antropov V P 2002 *J. Appl. Phys.* **91** 8540