Correlation between electron spin resonance and magnetization in Gd_5Ge_4

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Electron spin resonance (ESR) across the field-induced antiferromagnetic (AFM) to ferromagnetic (FM) transition in Gd_5Ge_4 has been studied. The AFM-FM transition can be characterized as an anomaly in the ESR spectrum. In the high-field FM state, a single strong ESR peak is observed while in the low-field AFM state, the ESR spectrum presents relatively weak double peaks. In the coexisting AFM and FM phases, the ESR spectrum is an asymmetrical double-peak structure due to a superposition of AFM and FM resonances. Thus, the ESR result is significantly correlated with magnetization. The g value for FM resonance is found to be close to $g=1.992$ for the free Gd^{3+} ion. The exchange interactions in the AFM state are discussed qualitatively.

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I. INTRODUCTION

Gd_5Ge_4 is an especially interesting material among the family of giant magnetocaloric $Gd_5(Si_{1-x}Ge_x)_4$.[1,2] In addition to the strong magnetocaloric and thermal effect,[3,4] many novel magnetic properties such as unusual training effect,[5] phase separation,[6] short-range ferromagnetic (FM) correlations,[7] and glasslike kinetically arrested state,[8] were revealed in the past few years. Gd_5Ge_4 is antiferromagnetic (AFM) below $T_N \sim 128$ K,[9–11] which was further identified by x-ray resonant magnetic-scattering measurements.[12] This AFM state is metastable and can be transformed into FM state accompanied by a simultaneous change in crystal structure of the compound,[13,14] depending on temperature, magnetic field, and pressure.[15,16] Generally, the AFM-FM transition is fully irreversible below ~10 K, partially reversible between ~10 and ~20 K, and entirely reversible above ~20 K.[9,17] It is believed that novel magnetic behavior observed in Gd_5Ge_4, in particular, the magnetocaloric effect, is associated with this first-order AFM-FM magnetostructural transition.

Recently, the origin of antiferromagnetism and ferromagnetism of Gd_5Ge_4 was investigated by band-structure calculation employing local spin-density approximation.[18,19] The AFM ground state as well as the first-order AFM-FM magnetostructural transition was clarified, indicating the importance of electronic structure in understanding the complexity of the magnetic behavior of Gd_5Ge_4. In addition to the theoretical work, electron spin resonance (ESR) is also a powerful tool to probe the magnetic interactions and correlations in a coupled spin system. Pires *et al.*[20] have reported a correlation of ESR with magnetization in $Gd_{5.09}Ge_{2.03}Si_{1.88}$, i.e., two coexisting phases associated with distinct crystallographic phases can be identified by ESR. A recent report on ESR of $Gd_5(Si_{1-x}Ge_x)_4$ system revealed a negative shift of paramagnetic (PM) effective g value for $Gd_{5.09}Ge_{2.03}Si_{1.88}$ and Gd_5Si_4, and a small positive one for Gd_5Ge_4.[21] The resultant exchange parameter between the localized Gd $4f$ spins and conduction electrons exhibits inverse variation—positive for the former two compounds and negative for Gd_5Ge_4. To date, data on ESR of $Gd_5(Si_{1-x}Ge_x)_4$ system are limited to Refs. 20 and 21, which reported the PM resonance collected at low fields and at a fixed frequency of 9.3 GHz. For Gd_5Ge_4, although the g value presents an upturn as the temperature approaches T_N and its exchange interaction parameter indicates a remarkable distinction from the other two compounds, these results cannot explain the low-temperature AFM character of Gd_5Ge_4.

In this paper, we report on the ESR measurements of Gd_5Ge_4 carried out at high fields and at high frequencies, which enables us to study both AFM and FM spin resonances. As a result, the ESR spectra different from those of the PM state were obtained. Our ESR spectra exhibit a single strong absorption peak in the FM state and two relatively weak peaks in the AFM state, showing a strong correlation between ESR and magnetic properties of Gd_5Ge_4. The exchange interactions in the AFM state are discussed qualitatively.

II. EXPERIMENTAL DETAILS

High-quality sample is crucial for carrying out ESR measurements. Our sample was taken from Ames Laboratory, USA. The details on the preparation of the polycrystalline sample of Gd_5Ge_4 as well as the x-ray powder-diffraction examination were described elsewhere.[4] The $M(H)$ curve measured at 4.2 K using a superconducting quantum interference device (SQUID) magnetometer presents a linear variation at low field (see the inset of Fig. 1), indicating a pure AFM character for the zero-field-cooled (ZFC) sample. Further increasing the field leads to a sharp AFM-FM transition at 2.5 T. For the ESR measurements performed in pulsed magnetic fields, the fine Gd_5Ge_4 powder (10 wt %) with its size well below the skin depth was mixed homogeneously with SiO_2 powder (90 wt %) to reduce possible eddy-current heating effects. The pulsed magnetic fields were generated by a coil driven by a 90 kJ capacitor bank.[22] The ESR data were collected by a spectrometer with operating frequencies of 65.4–300 GHz and at a temperature range

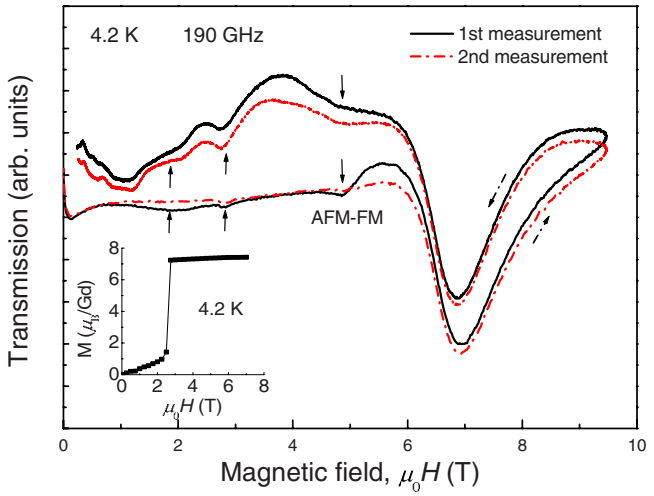

FIG. 1. (Color online) ESR spectra recorded at 190 GHz and 4.2 K in the ZFC and the following second measurements without warming the sample. The down arrows show the AFM-FM transitions. The other two anomalies are marked by the up arrows. The dash dot arrows show the direction of the variation in the magnetic field. The inset is the ZFC $M(H)$ curve measured using SQUID.

of 4.2–45 K. In the first measurement, the sample was warmed well above 30 K to remove any possible residual (arrested) FM state[17] and then ZFC to the desired temperature. The second measurement was performed approximately 10 min after completion of the ZFC measurement (waiting time is needed for cooling the magnet) without warming the sample.

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the ESR spectra of Gd_5Ge_4 collected at 190 GHz. In the ZFC measurement, there exists a small anomaly at low field in the H-increasing curve, which is marked by the down arrows in the figures. As temperature rises (see Fig. 2), the critical field for this anomaly decreases and reaches a minimum of 2.70 T around ~10 K. Above ~20 K, it presents a rapid increase. The critical field at 4.2 K is estimated to be ~4.8 T, which is in good agreement with the character field for the AFM-FM transition obtained in our recent $M(H)$ measurement in pulsed fields.[4] This anomaly is thus considered a field-induced AFM-FM transition. We note that the transition field is much larger than that derived in the conventional $M(H)$ measurement (see the inset of Fig. 1) because of the very large-field sweep rate in a pulsed field, which was well addressed in our recent report.[4] In the H-decreasing process (see Fig. 1), the anomaly associated with the FM-AFM transition is still observed but becomes relatively smooth, showing that a small amount of FM state is converted into the AFM state. This partial reversibility of the AFM-FM transition is due to the magnetocaloric effect under pulsed field.[4] In the second H-increasing measurement at 4.2 K (see Fig. 1), the AFM-FM transition becomes confused because most of the sample is in the FM state after the first measurement.[4] It is worth noting that there are another two anomalies in the ZFC AFM state marked by

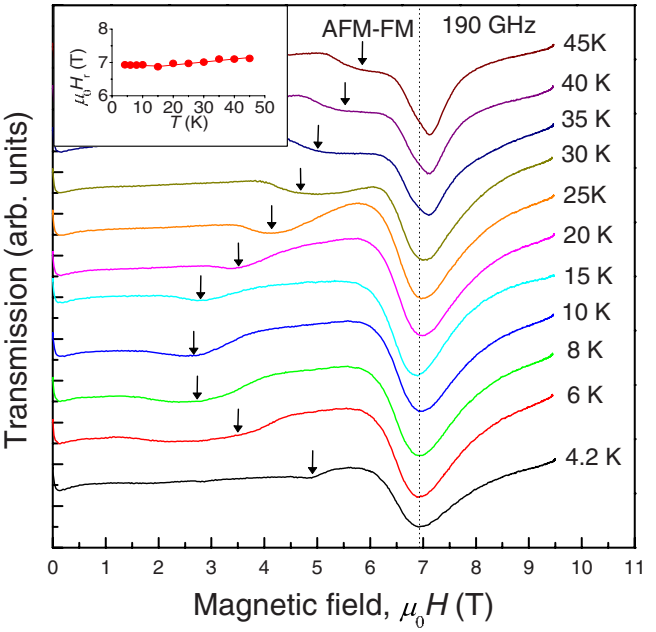

FIG. 2. (Color online) Temperature dependencies of ESR spectra measured at 190 GHz in the H-increasing process. The down arrows show the AFM-FM transitions. The inset is the resonance field as a function of temperature.

the up arrows in Fig. 1. One is still observed while the other becomes confused in the H-decreasing and the second H-increasing measurements. When decreasing the frequency, these two anomalies still exist and their positions are independent of field sweep rate, as shown in Fig. 3. The two anomalies might be identified as a higher-order transition of $\Delta S_z = 2$ based on the frequency-field dependence (see below).

In addition to the small low-field anomalies, a very strong peak is observed at higher field. At low temperatures, the character field for the peak is well above the critical field for

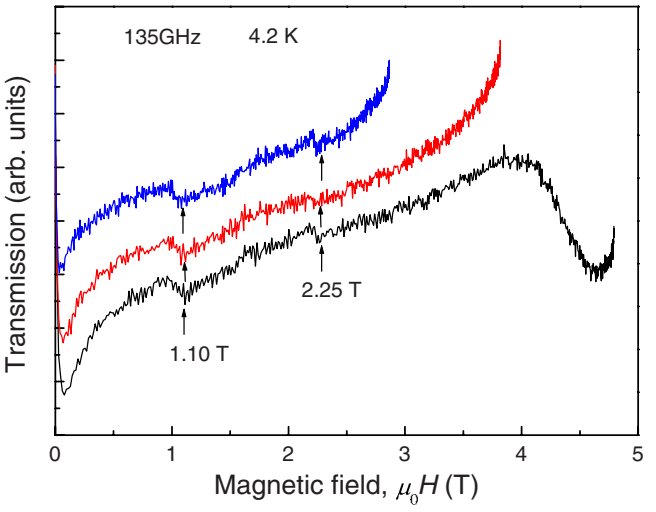

FIG. 3. (Color online) Temperature dependencies of ESR spectra measured at 135 GHz and 4.2 K in the H-increasing process. The data were collected using three different pulsed fields corresponding to different field sweep rates. The up arrows show the anomalies.

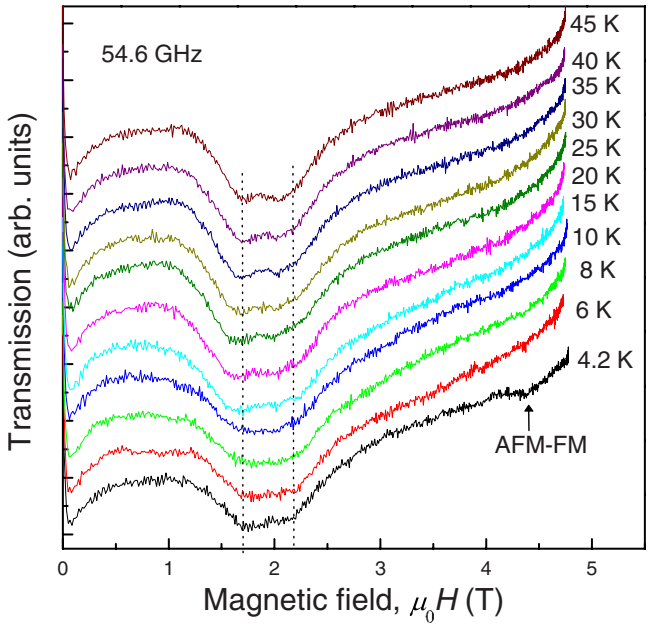

FIG. 4. (Color online) Temperature dependencies of ESR spectra measured at 54.6 GHz in the H-increasing process. The arrow shows the AFM-FM transition at 4.2 K. The dotted lines show the fields for the AFM resonances.

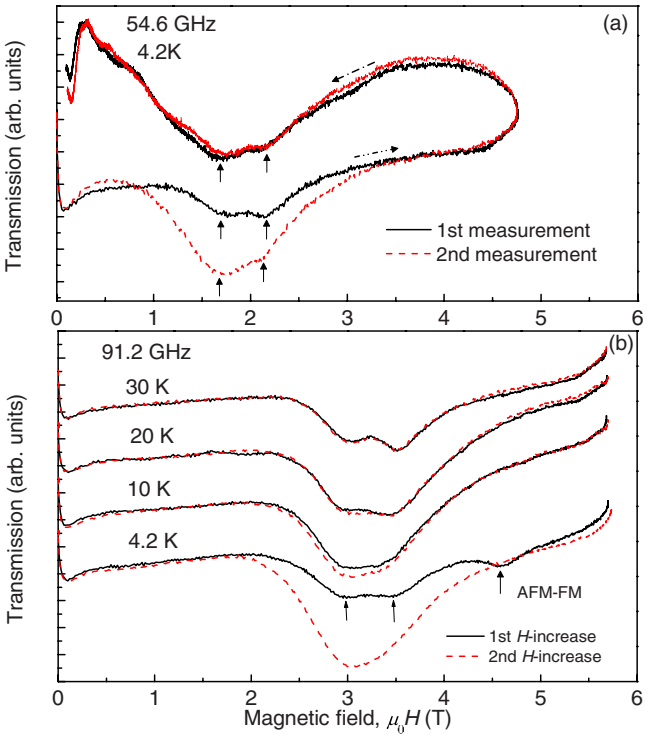

FIG. 5. (Color online) ESR spectra recorded in the ZFC and the following second measurements without warming the sample. The dash dot arrows show the direction of the variation in the magnetic field. (a) ω=54.6 GHz and T=4.2 K; (b) ω=91.2 GHz and T=4.2, 10, 20, and 30 K.

the AFM-FM transition, thus the peak can be ascribed to an FM resonance. Note that in some cases, e.g., $Nd_{1-x}Ca_xMnO_3$, the ESR spectra in the FM state may present a double-peak structure due to the weak FM coupling between the Nd ion and the ferromagnetically coupled Mn ions.[23] Hence, the single strong ESR peak observed in this study shows that our sample of Gd_5Ge_4 is in a pure FM state after the completion of the AFM-FM transition.

Figure 2 shows that with increasing temperature, the FM resonance field H_r remains nearly constant below 20 K but exhibits a significant shift toward higher field above ~20 K (see also the inset of Fig. 2) accompanied by a clear reduction in peak width. More importantly, above ~30 K, the ESR spectra present pronounced asymmetry, signing the existence of the other ESR peak. Note that above ~30 K, the curve after the AFM-FM transition clearly decreases in magnitude compared to that before the transition, in contrast to that below ~30 K. This suggests that the field-induced AFM-FM transition is not complete, i.e., a fraction of sample remains in the AFM state when the resonance occurs. Thus, the asymmetry of the ESR peak above ~30 K is closely related to the existence of AFM state or coexistence of the AFM and FM states. We note that the two-peak structure of ESR was often observed in the canted AFM state in manganites.[24,25] In addition, double-peak structure can be observed due to long-range structural or magnetic phase inhomogeneities (e.g., FM clusters), as revealed in $La_{1-x}Ca_xMnO_3$ and $La_{1.35}Sr_{1.65}Mn_2O_7$,[26,27] or to a coexistence of two different magnetic and crystallographic phases, as observed in $Gd_{5.09}Ge_{2.03}Si_{1.88}$.[20]

To further clarify the origin of the asymmetry of the ESR peak, we performed ESR measurements in AFM state. Figure 4 shows the ZFC ESR spectra measured at 54.6 GHz, at which the values of H_r for all curves are expected to be smaller than 2.70 T, the lowest field for the AFM-FM transition. It is quite clear that two distinct ESR peaks with a separation of ΔH_r=0.5 T are observed in the AFM state. Both ESR peaks do not exhibit detectable shift with increasing temperature. Since our ZFC sample is composed of nearly pure AFM phase with negligible residual FM component (see the inset of Fig. 1), we infer that the distinct two ESR peaks in the AFM state originate not from the phase separation but from AFM resonance of distinct AFM spin system of Gd_5Ge_4, in which the FM-ordering Gd moments in one slab are coupled by an AFM exchange to the FM-ordering Gd moments of the neighboring slab. In this sense, the asymmetrical ESR spectra above ~30 K (see Fig. 2) are the superposition of two AFM resonances and an FM resonance.

The superposition of two AFM resonances and an FM resonance is further supported by the ZFC ESR measurement followed by a second measurement without warming the sample, as shown in Fig. 5(a). Since the AFM-FM transition is not complete under present applied maximum field of 4.8 T, the sample should be a mixture of AFM and FM states after the ZFC measurement in pulsed fields. This can be seen in the H-decreasing measurement, where the low-field peak is enhanced due to the contribution of FM phase. Figure 5(a) also shows that compared to the ZFC ESR spectra, the spectra for the second measurement is greatly enhanced but still present two-peak structure, suggesting again a coexistence of AFM and FM states, in good agreement with the H-de-

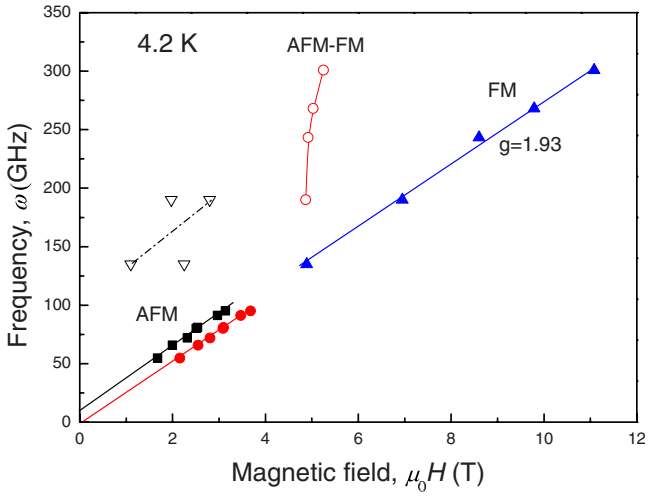

FIG. 6. (Color online) Frequency-resonance field plot at 4.2 K. The fields for the AFM-FM transition and the two anomalies observed in Figs. 1 and 3 are also plotted. The solid lines are the linear least-squares fittings.

creasing measurement. It is worth noting that the enhancement of the ESR spectra occurs mostly in the low-field peak, which suggests the FM character of this peak. Note that two AFM resonances, a strong quasi-FM mode and a weak quasi-AFM mode, were observed below T_N in the single crystal of $La_{1-x}Sr_xMnO_3$.[24] This can be well explained by the canted AFM magnetic structure within the framework of two-sublattice model. Recalling that in the spin-flop state ($H > 0.8$ T) of Gd_5Ge_4, the spin of Gd in each sublattice is slightly tilted away from the AFM coupling axis due to the application of magnetic field,[28] the low-field peak of the ESR spectra might be denoted as quasi-FM mode. To understand this phenomenon deeply, ESR spectra of single crystal are needed.

The enhancement of the ESR spectra in the low-field peak is further evidenced by the ZFC and the following second ESR measurements performed at 91.2 GHz, as shown in Fig. 5(b). As temperature rises, this enhancement is rapidly decreased and ultimately disappears above ~20 K, corresponding to the disappearance of FM component. It was reported that the residual FM state obtained in the second $M(H)$ measurement exhibits a decrease at ~10 K and nearly vanishes at ~22 K,[17] in accordance with our observation.

Based on the results presented above, the temperature dependence of the field-induced AFM-FM transition is characterized by the evolution of ESR spectra with temperature. Gd_5Ge_4 exhibits a strong FM resonance in the FM state and two relatively weak AFM resonances in the AFM state. In the coexisting AFM and FM phases, the asymmetrical double-peak feature of the ESR spectra (Figs. 2 and 5) originates from a superposition of two AFM resonances and an FM resonance. Thus, the observation of ESR correlates closely with the magnetization of Gd_5Ge_4.

The frequency-field dependence ($H_r-\omega$) of ESR measured at 4.2 K is shown in Fig. 6, where the field for the AFM-FM transition is also plotted. In the FM state, the resonance field H_r is proportional to the frequency. A linear least-squares fitting gives $g=1.93$ assuming that all the spins in the FM state maintain perfect parallelism during precession. Thus, the g values obtained here are much closer to that for noninteracting Gd^{3+} ion ($g=1.992$), which is very surprising because strictly speaking, it is very difficult to obtain the exact g value due to the demagnetization factor and magnetic anisotropy in an ordered phase. However, since our sample is fine powder, effects from the demagnetization factor and magnetic anisotropy might be partially removed. Extrapolation of the $H_r-\omega$ curve to zero frequency give a very small field, showing that the anisotropic energy is indeed small. Hence, the g value obtained here should be a good approximation.

In the AFM state, the values of H_r for both AFM resonances exhibit linear variation with nearly the same slope as that of $H_r-\omega$ curve in the FM state. The distance between the two resonances remains a constant of $\Delta H_r=0.5$ T. However, the polycrystalline sample used in this study prevents us from obtaining the g value and exchange interaction. One assumes that g remains unaltered (i.e., identical to that of FM state) and the anisotropic energy is small; each powder particle behaves like a single crystal and all the fine powder can rotate freely toward the field direction. Based on the Kittel's[29] formula on AFM resonance for a uniaxial antiferromagnet with the magnetic field along the easy axis, we obtain $H_A(H_A+2H_E)=1/16$ T^2 for $\Delta H_r=0.5$ T at 4.2 K. Since the anisotropic energy H_A is small, the exchange energy between the slabs, H_E, is expected to be very large, resulting in an AFM ground state of Gd_5Ge_4. Figure 4 shows that both H_{r1} and H_{r2} do not present significant shift (i.e., ΔH_r is a constant) as temperature rises, suggesting that exchange interaction remains essentially unaltered within a wide temperature range of 4.2–45 K. To determine the exact value of H_E, the ESR measurements of Gd_5Ge_4 single crystal are desired.

Finally, we also plot the character fields associated with the two anomalies observed in Figs. 1 and 3. It can be seen that the slope of the straight line connecting the low-field anomaly at 135 GHz and the high-field anomaly at 190 GHz is apparently smaller than those of the $H_r-\omega$ curves in the AFM and the FM states. This may suggest that the two anomalies originate from a higher-order transition of $\Delta S_z=2$.

IV. CONCLUSIONS

In summary, we have studied the variation in ESR spectra of Gd_5Ge_4 with temperature using high frequencies and pulsed high magnetic fields. We found that the ESR significantly correlates with magnetization. First, the field-induced AFM-FM transition is observed as an anomaly with a character field decreasing below ~10 K and increasing above 20 K, in good agreement with the magnetization measurements. Second, the ESR spectrum presents a single strong peak in the high-field FM state, two relatively weak peaks in the low-field AFM state, and an asymmetrical double-peak structure in the coexisting AFM and FM phases. The frequency-resonance field curve of the AFM state exhibits nearly the same slope as that of the FM state. The g value derived from FM resonances is close to $g=1.992$ for the free Gd^{3+} ion.

The exchange interaction in the AFM phase is discussed qualitatively.

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[1] V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[2] V. K. Pecharsky and K. A. Gschneidner, Jr., Appl. Phys. Lett. **70**, 3299 (1997).
[3] F. Casanova, A. Labarta, X. Batlle, F. J. Pérez-Reche, E. Vives, L. Mañosa, and A. Planes, Appl. Phys. Lett. **86**, 262504 (2005).
[4] Z. W. Ouyang, H. Nojiri, S. Yoshii, G. H. Rao, Y. C. Wang, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **77**, 184426 (2008).
[5] M. Manekar, M. K. Chattopadhyay, R. Kaul, V. K. Pecharsky, and K. A. Gschneidner, Jr., J. Phys.: Condens. Matter **18**, 6017 (2006).
[6] V. Hardy, S. Majumdar, S. Crowe, M. R. Lees, D. McK. Paul, L. Hervé, A. Maignan, S. Hébert, C. Martin, C. Yaicle, M. Hervieu, and B. Raveau, Phys. Rev. B. **69**, 020407(R) (2004).
[7] Z. W. Ouyang, V. K. Pecharsky, K. A. Gschneidner, Jr., D. L. Schlagel, and T. A. Lograsso, Phys. Rev. B **74**, 094404 (2006).
[8] S. B. Roy, M. K. Chattopadhyay, P. Chaddah, J. D. Moore, G. K. Perkins, L. F. Cohen, K. A. Gschneidner, Jr., and V. K. Pecharsky, Phys. Rev. B **74**, 012403 (2006).
[9] E. M. Levin, K. A. Gschneidner, Jr., and V. K. Pecharsky, Phys. Rev. B **65**, 214427 (2002).
[10] C. Magen, L. Morellon, P. A. Algarabel, C. Marquina, and M. R. Ibarra, J. Phys.: Condens. Matter **15**, 2389 (2003).
[11] F. Casanova, A. Labarta, X. Batlle, J. Marcos, L. Mañosa, A. Planes, and S. de Brion, Phys. Rev. B **69**, 104416 (2004).
[12] L. Tan, A. Kreyssig, J. W. Kim, A. I. Goldman, R. J. McQueeney, D. Wermeille, B. Sieve, T. A. Lograsso, D. L. Schlagel, S. L. Budko, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **71**, 214408 (2005).
[13] V. K. Pecharsky, A. P. Holm, K. A. Gschneidner, Jr., and R. Rink, Phys. Rev. Lett. **91**, 197204 (2003).
[14] Ya. Mudryk, A. P. Holm, K. A. Gschneidner, Jr., and V. K. Pecharsky, Phys. Rev. B **72**, 064442 (2005).
[15] L. Morellon, J. Blasco, P. A. Algarabel, and M. R. Ibarra, Phys. Rev. B **62**, 1022 (2000).
[16] C. Magen, Z. Arnold, L. Morellon, Y. Skorokhod, P. A. Algarabel, M. R. Ibarra, and J. Kamarad, Phys. Rev. Lett. **91**, 207202 (2003).
[17] H. Tang, V. K. Pecharsky, K. A. Gschneidner, Jr., and A. O. Pecharsky, Phys. Rev. B **69**, 064410 (2004).
[18] D. Paudyal, V. K. Pecharsky, K. A. Gschneidner, Jr., and B. N. Harmon, Phys. Rev. B **75**, 094427 (2007).
[19] D. Paudyal, V. K. Pecharsky, and K. A. Gschneidner, Jr., J. Phys.: Condens. Matter **20**, 235235 (2008).
[20] M. J. M. Pires, A. M. G. Carvalho, S. Gama, E. C. da Silva, A. A. Coelho, and A. M. Mansanares, Phys. Rev. B **72**, 224435 (2005).
[21] M. J. M. Pires, A. M. Mansanares, E. C. da Silva, A. M. G. Carvalho, S. Gama, and A. A. Coelho, Phys. Rev. B **73**, 144404 (2006).
[22] H. Nojiri, K.-Y. Choi, and N. Kitamura, J. Magn. Magn. Mater. **310**, 1468 (2007).
[23] F. Dupont, F. Millange, S. de Brion, A. Janossy, and G. Chouteau, Phys. Rev. B **64**, 220403(R) (2001).
[24] A. A. Mukhin, V. Y. Ivanov, V. D. Travkin, A. Pimenov, A. Loidl, and A. M. Balbashov, Europhys. Lett. **49**, 514 (2000).
[25] D. Talbayev, L. Mihály, and J. Zhou, Phys. Rev. Lett. **93**, 017202 (2004).
[26] M. T. Causa, M. Tovar, A. Caneiro, F. Prado, G. Ibanez, C. A. Ramos, A. Butera, B. Alascio, X. Obradors, S. Pinol, F. Rivadulla, C. Vazquez-Vazquez, A. Lopez-Quintela, J. Rivas, Y. Tokura, and S. B. Oseroff, Phys. Rev. B **58**, 3233 (1998).
[27] O. Chauvet, G. Goglio, P. Molinie, B. Corraze, and L. Brohan, Phys. Rev. Lett. **81**, 1102 (1998).
[28] Z. W. Ouyang, V. K. Pecharsky, K. A. Gschneidner, Jr., D. L. Schlagel, and T. A. Lograsso, Phys. Rev. B **76**, 134415 (2007).
[29] F. Keffer and C. Kettel, Phys. Rev. **85**, 329 (1952).