Freezing of magnetic moments in $(Zn_{1-x}Mn_x)_3As_2$ near 200 K

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Magnetic properties of the semimagnetic semiconductor $(Zn_{1-x}Mn_x)_3As_2$ (for short, ZMA) with $0.001 \le x \le 0.13$ have been investigated at temperatures between 4 and 300 K. It is shown that the magnetic susceptibilities of the samples cooled in zero external field (ZFC) and in a field (FC) are different for compositions with $x \ge 0.02$. At Mn concentrations $0.08 \le x \le 0.13$ freezing of the moments is observed around $T_f \sim 200$ K. When increasing the field from a few oersteds to 90 Oe a gradual smearing out of the maximum in the ZFC susceptibility and decreasing of T_f take place. The ac susceptibility data show a broad cusp at the freeezing temperature. These properties have a resemblance to the magnetic behavior of spin glasses. A spin-glass transition has been earlier reported in ZMA below 4 K by Denissen *et al.* [Phys. Rev. B **36**, 5316 (1987)]. The existence of two spin-freezing phenomena in the same material at very different temperatures is an uncommon feature and may be attributed to the complex structure of ZMA.

I. INTRODUCTION

$(Zn_{1-x}Mn_x)_3As_2$ (ZMA) is an open-gap, $E_g \simeq 1$ eV, *p*-type II-V semiconductor. At room temperature the crystal structure of pure Zn_3As_2 ($x=0.0$) is tetragonal with space group $I4_1cd$ (so-called α phase of Cd_3As_2).[1] The structure of ZMA with x at least up to 0.135 has been reported to be isomorphic to Zn_3As_2 between 4.2 and 300 K.[2] In these solid-solution Zn atoms are substituted by Mn. When the manganese concentration is increased to more than 15 at.%, a growing amount of inhomogeneities will appear in the form of a $ZnMn_2As_2$ phase,[3] according to metallographic, thermographic, and x-ray investigations.[4]

ZMA belongs to diluted magnetic semiconductors (DMS's). As observed already ten years ago,[5] many DMS's undergo a spin-glass transition at low temperatures. Their magnetic and other properties have been reviewed, for example, by Brandt and Moshchalkov.[6] It is obvious from a number of investigations that the spin-freezing transition can be observed even when the content of magnetic ions, e.g., in $Hg_{1-x}Mn_xTe$,[7] $Pb_{1-x}Mn_xTe$,[8] $Cd_{1-x}Mn_xTe$,[9] $Cd_{1-x}Mn_xSe$,[10] and $(Cd_{1-x}Mn_x)_3As_2$ (Ref. 11) is extremely small. Therefore a rather long-range magnetic interaction is likely to be responsible for the spin-glass freezing. Magnetic and specific-heat measurements have revealed a low-temperature spin-glass phase also in ZMA.[12] For the concentration range $0.005 \le x \le 0.14$, the freezing temperature was found to lie in the range $0.035 \le T_f \le 4.3$ K, respectively.[12]

Denissen *et al.*[12] measured the temperature dependence of the magnetic susceptibility of ZMA in a field of 1.2 T. The results showed an antiferromagnetic interaction with a long-range component between the manganese ions. The magnetic interactions are isotropic to a good approximation.[13] In order to obtain a more complete picture of the behavior of ZMA, it is important to investigate this system in weak fields over a wide temperature range. Considering the large size and complexity of the unit cell, this material is expected to show a number of interesting magnetic features, as evidenced by our preliminary experiments.[14]

We have measured different dc and ac magnetic properties of ZMA for the range of concentrations $0 \le x \le 0.13$. Our results give evidence for freezing of moments in samples with $x \ge 0.08$ at temperatures around 200 K. The behavior of this material is complex depending, for instance, on the thermal and magnetic history of the sample.

II. EXPERIMENTAL METHODS

Single crystals of ZMA were grown by the modified Bridgman method (slow cooling in the presence of a temperature gradient). Previously synthesized stoichiometric amounts of Zn_3As_2 and Mn_3As_2 were sealed in a carbon-coated evacuated quartz ampule and put into a vertical furnace. The crystal-growing temperature was adjusted according to Ref. 3. The speed of cooling was ≈ 1 °C/h in the region of crystallization temperatures and near the temperature of the β to α phase transition (see the Zn_3As_2-Mn_3As_2 phase diagram given in Ref. 4). With this method single crystals of ZMA were obtained in the range $0.0 \le x \le 0.13$. Monocrystallicity, composition, and homogeneity of the grown material were investigated by x-ray techniques. All crystals had the α-phase Cd_3As_2 structure at 300 K and were homogeneous. An additional argument for the good quality of the samples is the very small variation of the hole concentration in different parts of the crystal (variation is less than 3%).

The dc magnetic measurements were made with a su-

perconducting quantum interference device (SQUID) magnetometer working in the temperature range 4–220 K. In this equipment the sample passes through two counterwound coils, inducing a signal proportional to its magnetic moment. The temperature of the sample was controlled with flowing helium gas and measured with an accuracy of 0.2% by using a carbon-glass thermometer. The external magnetization field was produced by a superconducting magnet (or by a copper coil). Before every measurement the remanent field in the sample space (usually 1–2 Oe) was determined with a small Pb cylinder and compensated by observing the value of the field at which the plot of M vs H changes its sign.

The investigations of the ac susceptibility were made with a mutual inductance bridge working at the driving frequency of 320 Hz. The values of the driving fields were 0.7 Oe for the $x=0.10$ and 0.13, 1.4 Oe for the $x=0.08$, and 3.5 Oe for the $x=0.05$ samples. The temperature was determined with an accuracy of 2 K.

III. EXPERIMENTAL RESULTS

Our measurements show that as long as the concentration of Mn ions in ZMA is relatively small ($x<0.02$) the temperature dependence of the dc susceptibility can be well expressed by the Curie-Weiss law $\chi=\chi_0+C/(T-\Theta)$. By fitting the data to this formula, the Curie temperatures $\Theta=0$, -0.94, -1.44, and -3.03 K were obtained for the specimens with $x=0.001$, 0.005, 0.01, and 0.02, respectively. Negative values of Θ indicate antiferromagnetic interactions between Mn ions.

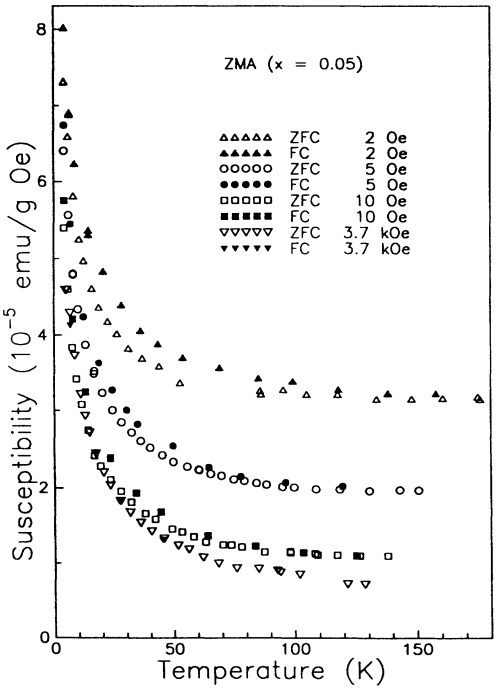

FIG. 1. ZFC (open symbols) and FC (solid symbols) susceptibilities of ZMA with $x=0.05$ vs temperature, measured in different magnetic fields.

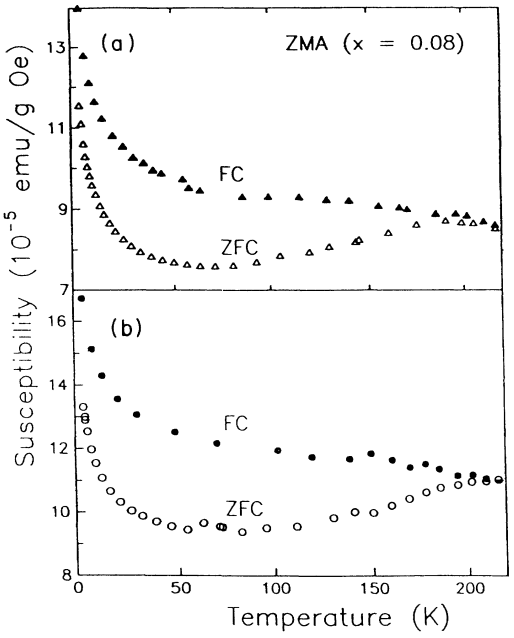

FIG. 2. ZFC and FC susceptibilities of ZMA with $x=0.08$ vs temperature in fields of (a) 50 Oe and (b) 5 Oe. The maximum on the ZFC curve in (a) is observed near 185 K.

However, careful investigations of the crystal with $x=0.02$ showed that in a weak external field the field-cooled (FC) and zero-field-cooled (ZFC) magnetizations are slightly different below 15 K.

In Fig. 1 are presented the dc susceptibility data of the sample with $x=0.05$. In order to see the influence of the applied field on the temperature dependence of χ_{dc}, the measurements were made in four different fields between 2 Oe and 3700 Oe. It is found that, for $H=2-10$ Oe, χ_{dc}(ZFC) and χ_{dc}(FC) start to differ below 120–70 K, respectively, depending on the value of H. Instead, when a

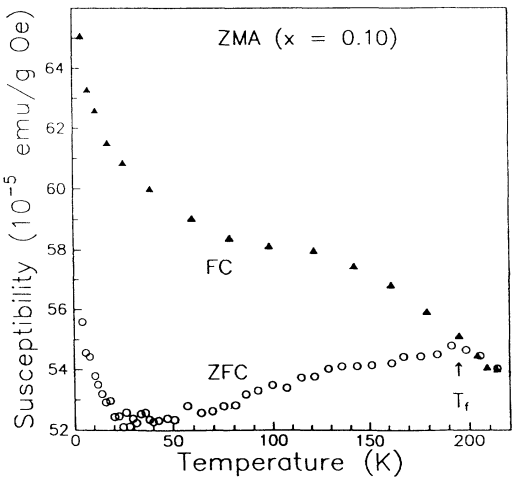

FIG. 3. ZFC and FC susceptibilities of ZMA with $x=0.10$ vs temperature in the field of 50 Oe.

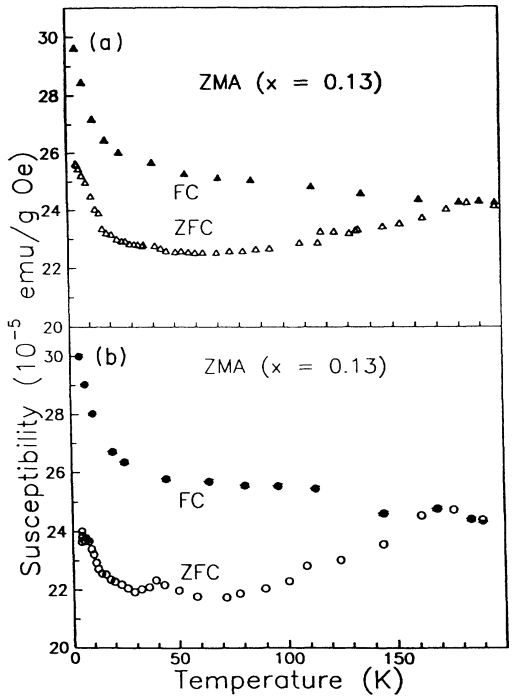

FIG. 4. ZFC and FC susceptibilities of ZMA with $x=0.13$ vs temperature in the fields of (a) 5 Oe and (b) 2 Oe.

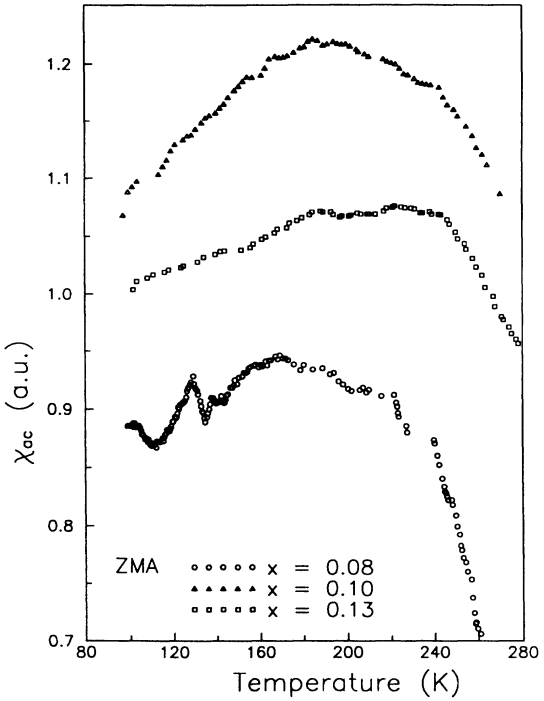

FIG. 6. ac susceptibility of ZMA with $x=0.08$ (circles), 0.10 (triangles), and 0.13 (squares) vs temperature.

strong field (3.7 kOe) is applied, no difference is observed. It is also evident that the magnetization of ZMA is large even at high temperatures in comparison with usual paramagnets.

The crystals with $x \geq 0.08$ exhibit a clear difference of χ_{dc}(ZFC) and χ_{dc}(FC) when measured in a weak field. As shown in Figs. 2–4, this phenomenon is observed below $T_f \approx 200$ K with evidence that the ZFC susceptibility attains a maximum near this temperature. The semiopen symbols at the highest temperatures denote the points where the ZFC data end and the FC data start. The measurement in a higher field revealed only an upturn of χ_{dc} when the temperature was lowered, as shown in Fig. 5 for $H=600$ Oe. The increase of the susceptibility at low temperatures is similar to what is observed in samples with low Mn concentration and can be ascribed to the Curie-Weiss behavior.[13,14]

The results presented above suggest that another freezing of magnetic moments takes place in ZMA well above the low-temperature spin-glass transition.[12] As shown in Fig. 6, low-field ac susceptibility has a cusp around T_f.

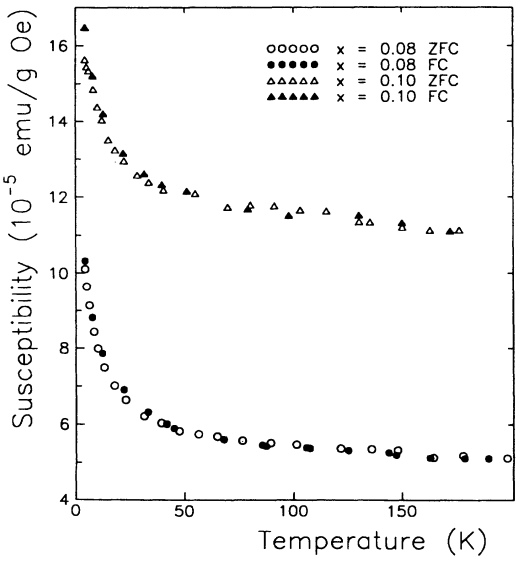

FIG. 5. ZFC (open symbols) and FC (solid symbols) susceptibilities of ZMA with $x=0.08$ (circles) and 0.10 (triangles) vs temperature in the field of 600 Oe.

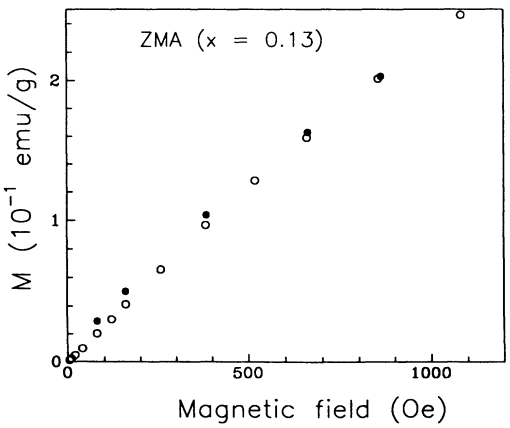

FIG. 7. Part of the hysteresis curve of ZMA with $x=0.13$, measured at 103 K with increasing (open symbols) and decreasing (solid symbols) the field.

The large width of the maximum of $\chi_{ac}(T)$ can be partly explained by the experimental conditions. Because of limitations imposed by the size of the sample and the sensitivity of the ac magnetometer, fields of $H_{ac} \geq 0.7$ Oe had to be applied in the measurement. The relatively high value of H_{ac} is likely to smear out the maximum of χ_{ac}. Nevertheless, the data of $\chi_{ac}(T)$ give additional support to the conclusion that the anomaly of $\chi_{dc}(T)$ of T_f is due to magnetic freezing. Obviously, the use of a high field (1.2 T) is the reason why this phenomenon was not observed in the earlier investigation of the magnetic properties of ZMA.[12]

In Fig. 7 is presented part of the hysteresis curve (for values of H, $0 \rightarrow +H_{max} \rightarrow 0$) of ZMA with $x=0.13$, measured at 103 K after cooling the sample in zero field. The hysteresis is weak, and the shape of the hysteresis curve is not compatible with a usual ferromagnetic order (constant in the cycle $H_{max} \rightarrow 0$), but rather with that of a spin glass.[15]

IV. DISCUSSION

One of the most prominent features of ZMA with $x \geq 0.05$ is the spin-glass-like dependence of its magnetic properties on the history of the sample. There are also several other reasons why the susceptibility anomaly at T_f pertains to a magnetic freezing phenomenon rather than to a phase transition. The existence of a complex quasiantiferromagnetic ordered phase has been reported for $Cd_{1-x}Mn_xTe$.[16] This phase is realized only at high concentrations ($x > 0.60$) and is not seen in the samples where the low-temperature spin-glass phase is present. It should also be noted that solid solutions of ZMA exist only up to $x=0.15$ and our experiments were made using even more dilute compositions. De Vries *et al.*[2] determined the crystal structure of this material by neutron-scattering measurements, but no observation of peaks attributable to magnetic ordering between 4 and 300 K was reported. It is known[2-4] that a large increase of Mn concentration in the ZMA lattice ($x > 0.15$) leads to growth of the $ZnMn_2As_2$ phase, which is ferromagnetic up to 317 K.[4] This phase was not detected in our samples or reported by other authors for similar compositions.[2,11] Moreover, in our recent investigations of $ZnMn_2As_2$ single crystals,[17] no magnetic anomaly was observed near $T_f \approx 200$ K. Similarly, the magnetic phase transitions of MnAs ($T_c \simeq 310$ K),[18] $Mn_{2.3}As$ ($T_c = 573$ K),[19] and Mn_3As_2 ($T_c = 273$ K) (Ref. 19) are far from the T_f observed by us. In chemical and μ-probe analysis, no traces of ferromagnetic impurities were found in the sample material.

The nature of the spin freezing in semimagnetic semiconductors has been a subject of controversy in the past. Recent investigations on $Cd_{1-x}Mn_xTe$ show that this and the related compounds undergo a spin-glass phase transition at a finite temperature, characterized by critical exponents.[20] Whether the critical scaling laws could be applied to the low-temperature spin freezing in ZMA (Ref. 12) is not known. Many of the magnetic properties of ZMA in weak fields, e.g., behavior of $\chi_{dc}(T)$ below T_f, the cusp in $\chi_{ac}(T)$, and the small hysteresis, are similar to those observed in spin glasses[15] and cluster glasses.[21] While referring to this similarity, we emphasize (without claiming that we have a true spin-glass transition) that our data can be qualitatively explained by freezing of magnetic clusters. A cluster model has been used earlier for ZMA in the form of the extended nearest-neighbor pair approximation (ENNPA),[12] but this approach neglects groupings larger than triplets.

Let us assume that a sample containing magnetic clusters is cooled down in conditions $H=0$. Then the clusters will freeze in with their moments oriented along the local anisotropy fields. If the magnetization is measured by using an applied field less than the anisotropy fields, it will grow with increasing temperature because the thermal excitations help the moments to orient themselves along the field. The susceptibilities of our ZFC samples with $x \geq 0.08$ obey this behavior when approaching T_f from the low-temperature side (see Figs. 2–4). During the FC procedure, the moments of the clusters will freeze according to correlations between the moments and the direction of the applied field. Because the local anisotropy fields remain the same, the magnetization (susceptibility) of the FC sample is expected to exceed that of the ZFC sample, as was observed in our experiments. Finally, if the applied field is stronger than the local anisotropy fields, it is able to align the moments already at low temperatures when the susceptibility measurement of the ZFC sample is started. As a result, no difference can be observed between χ_{dc}(ZFC) and χ_{dc}(FC), in agreement with the results in Fig. 5.

The occurrence of two magnetic freezing phenomena in the same material at very different temperatures is an uncommon feature. In ZMA it may be related to the complex structure of the material. The tetragonal unit cell contains 160 atoms and is built of 16 fluorite cubes. Each cube has 4 As atoms on a face-centered-cubic lattice (fcc lattice constant $\simeq 5.9$ Å) and 6 Zn/Mn atoms on a distorted simple cubic lattice (sc lattice constant $\simeq 2.45$ Å) with two vacancies connected by a body diagonal.[2] With some nonrandom distribution of Mn, it would be possible to have large clusters in this structure. The broad maxima in the $\chi_{ac}(T)$ curves shown in Fig. 6 suggests that the distribution of the size (coupling strength) of the freezing clusters is wide. Some of them can exist in temperatures considerably above T_f defined from the measurements of the static susceptibility.

After completing the experimental part of this work, we received a piece of the sample used in the earlier investigations of ZMA.[12] In this material the behavior of χ_{dc}(FC) and χ_{dc}(ZFC), as well as the value of T_f, was similar to what was observed in our samples. This suggests that the results reflect intrinsic properties of ZMA rather than artifacts due to miscellaneous magnetic impurities, inhomogeneity of the crystals, or differences in their thermal treatment, etc.

V. CONCLUSIONS

Magnetic properties of the semimagnetic semiconductor $(Zn_{1-x}Mn_x)_3As_2$ with $x \leq 0.13$ have been investigated over a wide range of temperatures and fields. The results

obtained for small manganese concentrations confirm the antiferromagnetic nature of the interactions between Mn ions in this compound.

A notable feature of our data is freezing of the magnetic moments much above the already known low-temperature spin-glass phase.[12] Slightly different dc susceptibilities of the samples cooled in zero magnetic field and in a field can be observed already at $x=0.02$. For compositions with $0.08 \leq x \leq 0.13$, the freezing temperature T_f is $\simeq 200$ K. Our results can be explained by assuming that below T_f frozen magnetic clusters with a large distribution of size are present in the samples.

The high-temperature freezing of the moments is not observable above a field which depends on the value of x (90 Oe for $x=0.10$). In this case the temperature dependence of the dc susceptibility has formal similarity to the Curie-Weiss behavior. However, the high-temperature plots of $1/\chi$ cannot be used to determine the Mn-Mn interactions in a straightforward manner because the magnetization has a significant contribution from the moments of the clusters.

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[1]A. Pietratszko and K. Lukaszewcz, Phys. Status Solidi A **18**, 723 (1973).
[2]G. C. De Vries *et al.*, Physica B **156&157**, 321 (1989).
[3]E. K. Arushanov *et al.* (unpublished).
[4]V. S. Zachvalinskiy *et al.*, Bull. Acad. Moldova **1**, 87 (1991).
[5]S. Nagata *et al.*, Phys. Rev. B **22**, 3331 (1980); R. R. Galazka *et al.*, *ibid.* **22**, 3344 (1980).
[6]N. B. Brandt and V. V. Moshchalkov, Adv. Phys. **33**, 193 (1984).
[7]N. B. Brandt *et al.*, Zh. Eksp. Teor. Fiz. **84**, 1050 (1983) [Sov. Phys. JETP **57**, 614 (1983)].
[8]M. Escorne *et al.*, Phys. Rev. B **29**, 6306 (1984).
[9]M. A. Novak *et al.*, J. Appl. Phys. **57**, 3418 (1985).
[10]M. A. Novak *et al.*, Physica B+C **126**, 469 (1984).
[11]C. J. M. Denissen *et al.*, Phys. Rev. B **33**, 7637 (1986).
[12]C. J. M. Denissen *et al.*, Phys. Rev. B **36**, 5316 (1987).
[13]R. Laiho *et al.*, in *Proceedings of 20th International Conference on the Physics of Semiconductors,* Thessaloniki, Greece, 1990, edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), Vol. 1, p. 759.
[14]E. Lähderanta *et al.*, J. Magn. Magn. Mater. **104-107**, 1605 (1992).
[15]S. Nagata *et al.*, Phys. Rev. B **19**, 1633 (1979); P. J. Ford, Contemp. Phys. **23**, 141 (1982).
[16]U. Steigenberger and L. Lindley, J. Phys. C **21**, 1703 (1988); T. Giebultowicz *et al.*, Phys. Scr. **25**, 731 (1982); U. Steigenberger, B. Lebech, and R. R. Galazka, J. Magn. Magn. Mater. **54-57**, 1285 (1986).
[17]A. N. Nateprov *et al.* (unpublished).
[18]A. Zieba, Y. Shapira, and S. Foner, Phys. Lett. **91A**, 243 (1982).
[19]J. S. Kouvel, in *Intermetallic Compounds,* edited by J. H. Westbrook (Wiley, New York, 1976), p. 545.
[20]D. Bertrand *et al.*, Phys. Rev. B **45**, 507 (1992).
[21]J. Vanhatalo and R. Laiho, Solid State Commun. **65**, 1207 (1988).