Spin-glass-like behavior and electrical transport properties of $Cr_7(Se_{1-x}Te_x)_8$

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The magnetic and electrical transport behaviors of $Cr_7(Se_{1-x}Te_x)_8$ compounds are investigated in detail. Spin-glass-like behavior is observed, which results from the spin frustration due to the competition between ferromagnetic and antiferromagnetic interactions. As Se is substituted by Te, a minimum of resistivity is observed in temperature dependence of resistivity and the temperature T_{min} corresponding to the minimum increases with Te concentration. Hopping conductivity in terms of variable range-hopping is used to describe the electrical transport behavior below T_{min}. The resistivity of these compounds is sensitive to the external magnetic field, which shifts the magnetic ordering temperature T_{MO} to higher temperature and T_{min} to lower temperature. The resistivity at the magnetic field becomes smaller, compared to the zero-field value, resulting in a negative magnetoresistance.

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Compounds of 3*d* transition metals with VIB elements (S, Se, Te) exhibit a variety of structural, optical, and thermal properties because of their interrelation and incomplete *d*-shell of the component transition metals.[1] In addition they have a good combination of both abnormal electrical and magnetic properties. As a consequence of this diversity they have excited considerable interest. It is known that Cr_7Se_8 has a monoclinic structure with an ordered arrangement of vacant chromium sites, which is antiferromagnetic with a Néel temperature T_N of about 162 K.[2] On the other hand, Cr_7Te_8 has the same crystal structure as Cr_7Se_8, which is ferromagnetic with a Curie temperature T_C of about 330 K.[3] Similar to the $Mn_{1-x}Cr_xTe$ system,[4] they have the same crystal structure and comparatively small difference in their lattice constants. In this work, we attempt to combine Cr_7Se_8 and Cr_7Te_8 together, expecting a complete solid solution in the $Cr_7(Se_{1-x}Te_x)_8$ system and unusual changes near $x=0.3$ since it orders ferromagnetically for $x>0.3$ as reported in Ref. 5. Meanwhile, Cr_7Se_8 appears to be a semiconductor, whereas Cr_7Te_8 is a metal conductor.[3] It is interesting to detect if there exist some abnormal electrical transport properties at a certain composition region. Hence, in this paper, the magnetic and electrical transport properties of $Cr_7(Se_{1-x}Te_x)_8$ compounds are investigated.

The specimens were prepared by the solid reaction of Cr (99.95%), Se (99.999%), and Te (99.999%) powders, which were mixed in the desired proportion and pressed into pellets. An excess (4 at. %) of Se and Te over the stoichiometric amount was added to compensate for their mass loss during sintering. The pellets were placed into Al_2O_3 crucibles that were sealed in an evacuated silica tube. The samples were heated at 250 °C for 24 h, followed by heating at 950 °C for 48 h. After cooling, they were pulverized, mixed, pressed into pellets, and heated again at 700 °C for 72 h, and then quenched in water. The temperature dependence of resistivity was recorded by a standard four-probe technique in the range of 350–5 K at a constant current of 1 mA. A superconducting quantum interference device (SQUID, Quantum Design) was employed to investigate the magnetic properties of the compounds.

The x-ray diffraction (XRD) patterns indicate that all the specimens are of a single phase with a monoclinic structure without other secondary phases. The $Cr_7(Se_{1-x}Te_x)_8$ system forms a complete solid solution in all range of x and basically, the lattice parameters a, b, and c increase with increasing x. The lattice parameters a and β show obvious abnormal changes, at the transition point ($x=0.3-0.4$) of the magnetism, which are similar to the previous results in Ref. 5.

The results of the magnetization measured warming up at a field of 50 Oe, after cooling down from room temperature first without an applied field [zero field cooled (ZFC)] (or with an applied field [field cooled (FC)]), are shown in Fig. 1(a) for $x=0.1$, 0.2, and 0.3. The low temperature behaviors are characterized by a maximum in ZFC signals at $T_f=20$, 40, and 45 K, respectively. Magnetic irreversibility can be observed and M_{ZFC} falls below M_{FC} at temperatures below T_f, behaviors observed in typical spin-glass (SG) materials.[6] The temperature dependence of ac susceptibility for $x=0.4$ and 0.5 was recorded with an ac field amplitude of 5 Oe and a frequency of 100 Hz, which exhibits peaks at 55 and 80 K [see the inset of Fig. 1(a)], respectively.

To further understand the apparent transition at T_f, we measured the frequency dependence of the susceptibility in the range 10–1000 Hz for $Cr_7Se_{5.6}Te_{2.4}$ compound. The sample was first cooled from 295 to 47 K without any applied magnetic field. Then it was heated, while measuring the susceptibilities for 10, 100, 500, and 1000 Hz simultaneously at each temperature. Just as shown in Fig. 1(b), the susceptibility becomes frequency dependent above the cusp at 49 K. With increasing frequency, χ has a reduced amplitude and the broad maximum shifts to higher temperatures, as commonly seen in classical spin-glass systems.[6] Because there is no further supporting data on specific heat, we associate our results with a spin-glass-like transition having a freezing temperature at T_f, which increases with the Te doping. For $Cr_7(Se_{1-x}Te_x)_8$ compounds, to obtain a spin-glass-like state, there must be a competition between ferromagnetic and antiferromagnetic interactions so that no single configuration of the spins is uniquely favored by all the interactions, which is commonly called frustration.[7] Further-
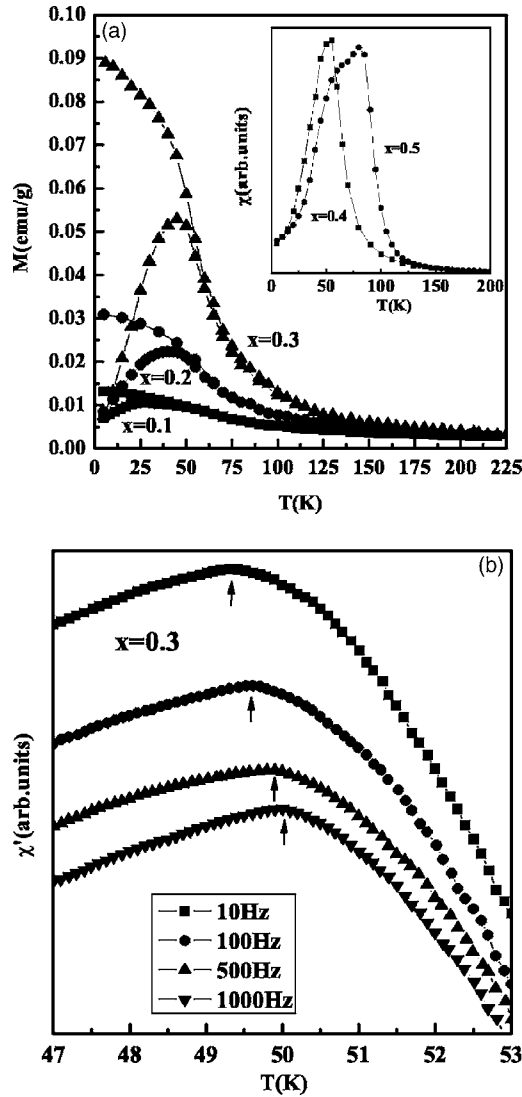
FIG. 1. (a) Field-cooled and zero-field-cooled magnetization of $Cr_7(Se_{1-x}Te_x)_8$ compounds for $x=0.1$, 0.2, and 0.3 in a dc field of 50 Oe (the inset shows the temperature dependence of the ac susceptibility of $Cr_7(Se_{1-x}Te_x)_8$ compounds for $x=0.4$ and 0.5 with an ac field amplitude of 5 Oe and a frequency of 100 Hz). (b) Frequency dependence of the susceptibility measured at 10, 100, 500, and 1000 Hz for the $Cr_7Se_{5.6}Te_{2.4}$ compound.

more, these interactions must be at least partially random.[7] In the $Cr_7(Se_{1-x}Te_x)_8$ system, the disorder of Se and Te atoms in the crystal lattice can introduce the randomly frustrated Cr-Cr exchange interactions, which is necessary for the occurrence of the spin-glass-like state. A similar mechanism exists in URh_2Ge_2,[8] where the spin-glass behavior was attributed to the structural disorder of Rh and Ge atoms.

Figure 2 represents the temperature dependence of resistivity for the $Cr_7(Se_{1-x}Te_x)_8$ compounds. For Cr_7Se_8 [see the inset of Fig. 2(a)], a metallic conducting behavior is clearly observed, in agreement with Ref. 9. An obvious change of slope in resistivity can be observed at about 160 K, which just corresponds to the Néel temperature ($T_N=162$ K).[2] The spin disorder scattering, i.e., scattering by magnons,[10] is responsible for the change of resistivity near T_N. When Se is

substituted by Te for $x=0.1$, interestingly, the resistivity $\rho(T)$ gradually decreases at low temperatures followed by an upturn below about 20 K, giving rise to a resistivity minimum at about $T_{min}=20$ K, which indicates a metal-insulator (M-I) transition. Similar phenomena are observed at 40, 85, 145, and 165 K for $Cr_7Se_{6.4}Te_{1.6}$, $Cr_7Se_{5.6}Te_{2.4}$, $Cr_7Se_{4.8}Te_{3.2}$, and $Cr_7Se_4Te_4$ compounds, respectively. For $Cr_7Se_{5.6}Te_{2.4}$ and $Cr_7Se_{4.8}Te_{3.2}$ [see Figs. 2(a) and 2(b)], kinks in the temperature dependence of resistivity around T_C (70 and 80 K, respectively) are still seen. As temperature is decreased to be below T_C, the resistivity increases rapidly. The observed negative slope of $\rho(T)$ can be accounted for hopping conductivity in terms of variable range hopping (VRH). In the three-dimensional case, the temperature-dependence of the hopping conductivity was derived by Mott as[11]

$$\sigma_{hc}(T) = \sigma_0 \exp(-A/T)^{1/4} \qquad (1)$$

where σ_0 is a material constant and A corresponds to a characteristic temperature of the system. As can be seen in Fig. 3, the natural logarithm of resistivities of the $Cr_7(Se_{1-x}Te_x)_8$ (shown in the figure for $x=0.3$ and 0.4) compounds are proportional to $T^{-1/4}(T<T_{min})$, which can be fitted well in terms of the VRH model [i.e., Eq. (1)]. Therefore the mechanism of variable range hopping is responsible for the unusual transport property at low temperatures. For $x=0.5$, the resistivity increases slowly below $T_{min\,1}$ and a hump can be seen around $T_C=110$ K. But different from $x=0.3$ and 0.4, the resistivity decreases rapidly below T_C and another minimum in resistivity can be observed at lower temperature $T_{min\,2}$ (about 20 K). It seems that there exists some competition between order and disorder, metal and nonmetal behaviors. According to Fig. 2, the width of the hopping conductivity range (from T_{min} to 5 K) is increased when the composition of the compounds deviates from the stoichiometry Cr_7Se_8 (5–20 K for $x=0.1$, 5–40 K for $x=0.2$, 5–80 K for $x=0.3$, and 5–145 K for $x=0.4$). Growing disorder, due to the solid solution, leads to an extension of the range. Thus the range of hopping conductivity is proportional to the atomic disorder in the crystal structure.[12]

Our data reveal the similar tendency between the composition dependence of the spin freezing temperature and the resistivity minimum temperature (T_f and T_{min} all increases with the doping of Te), which is similar to the $La_{2-x}Sr_xCuO_4$ system.[13] The similarity indicates the association between spin disorder state and electronic transport. A resistivity minimum near T_f has been observed in a number of other concentrated d- and f-electron spin glasses. Similar behavior was observed near the spin-glass transition in $La_{2-x}Sr_xCuO_4$,[13] Ni-Mn-Pt alloy,[14] $FeAl_2$ alloy,[15] and U_2PdSi_3 (Ref. 7) systems. Panagopoulos and Dobrosavljević[13] suggested that the spin freezing induces the charge retardation and lowers the charge mobility and intrinsic disorder plays a key role in the metal-insulator transition. We believe that in the $Cr_7(Se_{1-x}Te_x)_8$ system, the glass characteristics make a significant role to the M-I transition. The correlation between resistivity and glassyness indicates that we are dealing with a strongly localized insulator displaying hopping transport property at $T<T_{min}$.
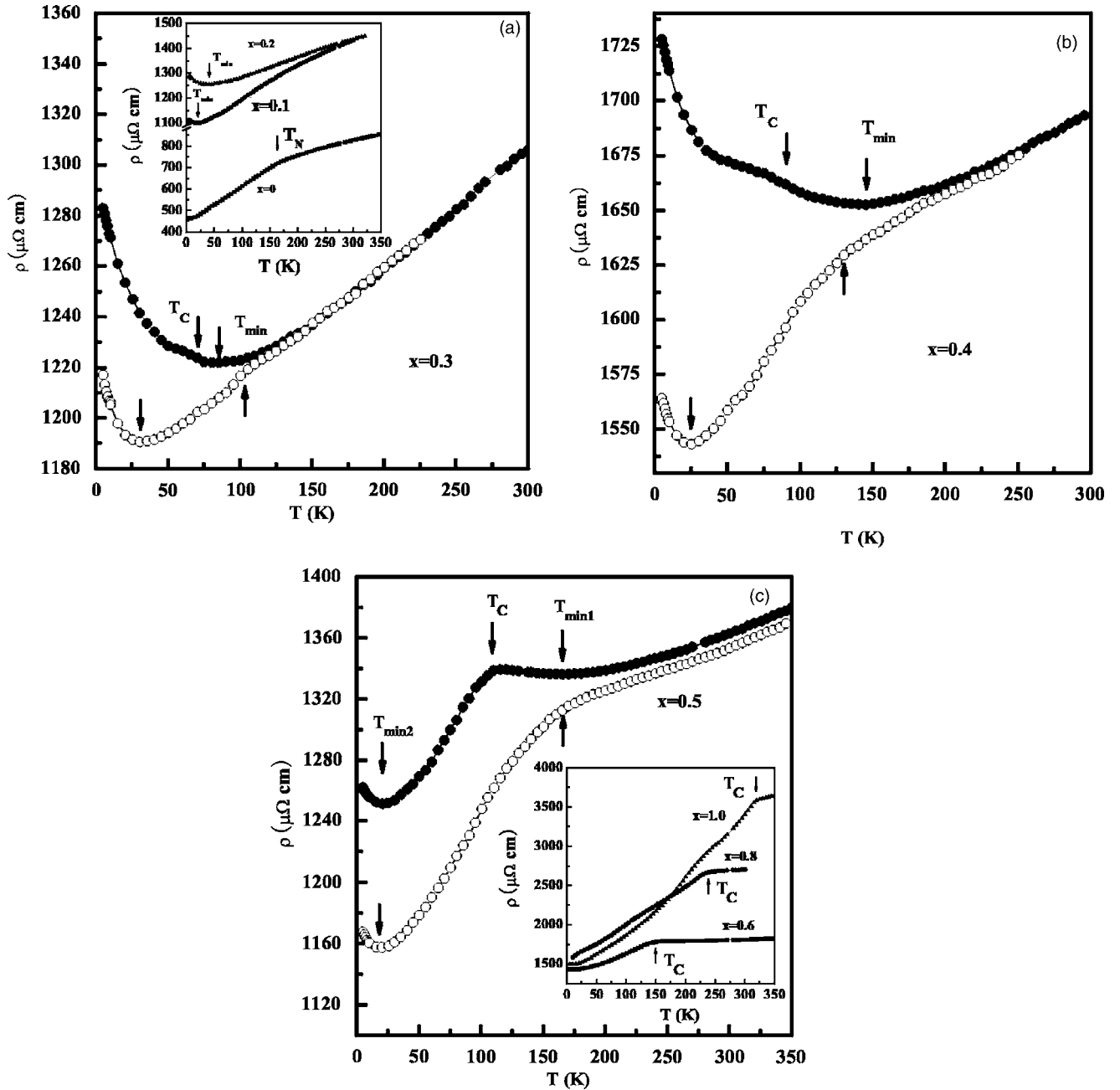
FIG. 2. Temperature dependence of resistivity of $Cr_7(Se_{1-x}Te_x)_8$ compounds for (a) $x=0.3$, (b) $x=0.4$, and (c) $x=0.5$ at zero field (the closed symbols) and an applied field of 50 kOe (the open symbols). The vertical arrows at higher temperature and lower temperature represent the T_{MO} (magnetic ordering temperature) and T_{min} under the magnetic field of 50 kOe, respectively. The insets of (a) and (c) show the temperature dependence of resistivity of $Cr_7(Se_{1-x}Te_x)_8$ compounds for $x=0$, 0.1, and 0.2 and $x=0.6$, 0.8, and 1.0, respectively.

Furthermore, we can see [in Figs. 2(a)–2(c)] that at the applied magnetic field, the magnetic ordering has a profound effect on the resistivity of the compounds. When an external magnetic field of 50 kOe is applied, the magnetic ordering temperature (T_{MO}) of these compounds ($x=0.3$, 0.4, and 0.5) shifts to higher temperature, but the T_{min} shifts to lower temperature, which can also be observed in $La_{0.5}Pb_{0.5}MnO_3$.[16,17] An applied magnetic field of 50 kOe suppresses the spin fluctuations, stabilizes the FM ordering state, and expands the FM state to a larger temperature region, which makes the magnetic ordering temperature higher. On the other hand, the

applied magnetic field may reduce the disorder in the crystal, alter the localization length resulting in an enhancement of the mobility of the electron cloud,[18] and finally narrow the hopping conductivity range. Thus the T_{min} shifts to lower temperature. In the temperature range of 30–85 K for $Cr_7Se_{5.6}Te_{2.4}$ and 25–145 K for $Cr_7Se_{4.8}Te_{3.2}$, there exists a field-induced nonmetal-metal transition below/at an applied field of 50 kOe. The resistivity in the field-induced metal state becomes smaller, compared to that in the zero-field nonmetallic state and this eventually results in the negative magnetoresistance (MR) [defined as $\mathbf{MR}=(\rho_H-\rho_0)/\rho_0$]. The
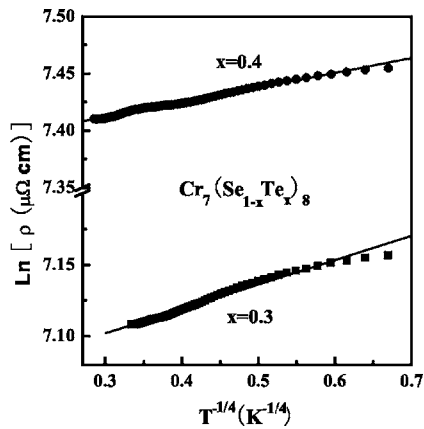
FIG. 3. Resistivity on a natural logarithmic scale as a function of $T^{-1/4}$ for the $Cr_7Se_{5.6}Te_{2.4}$ and $Cr_7Se_{4.8}Te_{3.2}$ compounds.

MR values at the field of 50 kOe are -5.2%, -7.6%, and -9.5% at 5 K for $Cr_7Se_{5.6}Te_{2.4}$, $Cr_7Se_{4.8}Te_{3.2}$, and $Cr_7Se_4Te_4$ compounds, respectively. Such effect may result from tunneling between magnetically coupled grains due to the polycrystalline nature of the samples. Hwang et al.[19] suggested that the role of spin-polarized tunneling at the polycrystalline grain boundaries should be important in magnetotransport behavior and the observed decrease in resistance is the result of the progressive alignment of the magnetic domains associated with the grains by the movement of the domain walls across the grain boundaries. Rozenberg et al.[16] also reported that in the $La_{0.5}Pb_{0.5}MnO_3$ system, the resistivity decreases upon applying magnetic fields due to the tunneling between coupled grains. The tunnel resistance decreases because application of the external magnetic field forces the grains to orient such that the carrier spins from the neighboring grains align favorably to reduce the energy gap.[17] Quantum interference effect (QIE) may also be non-negligible in the transport properties of our disordered $Cr_7(Se_{1-x}Te_x)_8$ compounds. A similar effect can be observed in $Nb_{5-\delta}Te_4$ (Ref. 20) and Ta_4Te_4Si (Ref. 21) singe crystals. With further increase of Te $(x > 0.5)$, the resistivity minimum effect disappears [see the inset of Fig. 2(c)], showing obviously a metallic conducting behavior with notable change in slope at about 325, 232, and 150 K, respectively, which just corresponds to the Curie temperatures of these compounds.

In summary, the magnetic and electrical transport properties of the $Cr_7(Se_{1-x}Te_x)_8$ compounds have been investigated. Spin frustration due to the competition between ferromagnetic and antiferromagnetic interactions results in the spin-glass-like behavior. When Se is substituted by Te, a minimum of resistivity is observed in the R-T curve and the corresponding temperature T_{min} increases with Te concentration. Hopping conductivity in terms of variable range-hopping describes successfully the electrical transport behavior below T_{min}. The external magnetic field shifts the magnetic ordering temperature T_{MO} to higher temperature and T_{min} to lower temperature and decreases the resistivity, resulting in a negative magnetoresistance.

[1] J. B. C. Efrem D'Sa, P. A. Bhobe, K. R. Priolkar, A. Das, S. K. Paranjpe, R. B. Prabhu, and P. R. Sarode, J. Magn. Magn. Mater. **285**, 267 (2005).

[2] T. Kaneko, J. Sugawara, K. Kamigaki, S. Abe, and H. Yoshida, J. Phys. (France) **24**, 443 (1963).

[3] K. Ozawa, T. Yoshimi, M. Irie, and S. Yanagisawa, Phys. Status Solidi A **11**, 581 (1972).

[4] Y. B. Li, Y. Q. Zhang, N. K. Sun, Q. Zhang, D. Li, J. Li, and Z. D. Zhang, Phys. Rev. B **72**, 193308 (2005).

[5] M. Yuzuri, T. Nakagawa, and M. Sugimoto, J. Magn. Magn. Mater. **104-107**, 885 (1992).

[6] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).

[7] D. X. Li, Y. Shiokawa, Y. Homma, A. Uesawa, A. Dönni, T. Suzuki, Y. Haga, E. Yamamoto, T. Honma, and Y. Ōnuki, Phys. Rev. B **57**, 7434 (1998).

[8] S. Süllow, G. J. Nieuwenhuys, A. A. Menovsky, J. A. Mydosh, S. A. M. Mentink, T. E. Mason, and W. J. L. Buyers, Phys. Rev. Lett. **78**, 354 (1997).

[9] V. A. Ivanova, D. SH. Abdinov, and G. M. Aliev, Phys. Status Solidi **24**, K145 (1967).

[10] P. G. De Gennes and J. Friedel, J. Phys. Chem. Solids **4**, 71 (1958).

[11] N. F. Mott, Philos. Mag. **22**, 7 (1970).

[12] B. Ya. Kotur, A. M. Palasyuk, E. Bauer, H. Michor, and G. Hilscher, J. Phys.: Condens. Matter **13**, 9421 (2001).

[13] C. Panagopoulos and V. Dobrosavljevic, Phys. Rev. B **72**, 014536 (2005).

[14] Hüseyin Zafer Durusoy and Yildirhan Öner, Phys. Rev. B **42**, 6831 (1990).

[15] C. S. Lue, Y. Öner, D. G. Naugle, and Joseph H. Ross, Jr., Phys. Rev. B **63**, 184405 (2001).

[16] E. Rozenberg, M. Auslender, I. Felner, and G. Gorodetsky, J. Appl. Phys. **88**, 2578 (2000).

[17] M. Battabyal and T. K. Dey, Physica B **367**, 40 (2005).

[18] R. Mallik, E. V. Sampathkumaran, M. Strecker, and G. Wortmann, Europhys. Lett. **41**, 315 (1998).

[19] H. Y. Hwang, S. W. Cheong, N. P. Ong, and B. Batlogg, Phys. Rev. Lett. **77**, 2041 (1996).

[20] A. Stolovits, A. Sherman, R. K. Kremer, Hj. Mattausch, H. Okudera, X. M. Ren, A. Simon, and J. R. O'Brien, Phys. Rev. B **71**, 144519 (2005).

[21] A. Stolovits, A. Sherman, K. Ahn, and R. K. Kremer, Phys. Rev. B **62**, 10565 (2000).