Thermoelectric properties of the semimetallic Heusler compounds $Fe_{2-x}V_{1+x}M$ (M=Al, Ga)

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We have studied the thermoelectric properties of the stoichiometric and off-stoichiometric Heusler compounds $Fe_{2-x}V_{1+x}M$ (M=Al, Ga) between 10 and 300 K. Seebeck coefficient (S) measurements indicate that stoichiometric Fe_2VAl and Fe_2VGa are p-type materials with moderate S values of about 30–40 μV/K at room temperature. Upon substituting the Fe site with V, a significant enhancement on Seebeck coefficients accompanied by a sign change are observed. On the other hand, the low-temperature resistivity (ρ) grows drastically with V substitution for Fe, while the thermal conductivity (κ) remains almost unaffected in the substitution levels we investigated. These features are consistent with other experimental results and are related to issues raised by band-structure calculations. The thermoelectric performance in these semimetallic Heusler compounds is estimated to be an order of magnitude lower than conventional thermoelectric materials.

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I. INTRODUCTION

Since the Skutterudite compounds were identified as promising candidates for advanced thermoelectric materials,[1] there is a growing interest in studying the thermoelectric performance of intermetallic systems. One of the groups that has been intensively investigated is the ternary half-Heusler compounds with MgAgAs structure. Materials of this type exhibiting semiconducting or semimetallic behavior were originally found in MNiSn (M=Zr, Hf, Ti).[3] Thermoelectric measurements on this system further indicated the possession of large Seebeck coefficients (S).[4,5] Experimental evidence suggested that the large Seebeck coefficient would be the common feature for the semiconducting or semimetallic half-Heusler compounds.[6–11] The observed high S values in the half-Heusler phases can be associated with the presence of small gaps or pseudogaps at their Fermi-level density of states (DOS) with a size of several tenth electron volts.

Half-Heusler alloys (MgAgAs type) with general formula XYZ (X and Y are transition elements; Z=Sn or Sb) are derived from the cubic $L2_1$ Heusler phase X_2YZ by removing one of the equivalent X atoms, leaving a vacancy site. Due to this empty site, X neighboring atoms are more distant ($d_{X-X}\sim$4.2 A) than in the Heusler alloys ($d_{X-X}\sim$3 A). Consequently, it leads to a weaker overlap of d-character wave functions in the half-Heusler alloys, which gives rise to narrow bands in DOS spectra. Since the XYZ systems are far from compact, they crystallize through covalent bonding, according to the chemical point of view. The ideal valence electron concentration (VEC) is 8 or 18 electrons per formula unit, which corresponds to MgAgAs, NiTiSn, CoTiSb, etc. Semiconducting behavior is usually found for VEC =18 in this family, but disappears for other values of VEC.

On the other hand, the Heusler-type compounds commonly appear as metals. However, semiconductinglike behavior was observed in Fe_2VAl and Fe_2VGa, as evidenced by their negative temperature coefficient of resistivity.[12–14] Several theoretical calculations[15–18] predicted the presence of a pseudogap in Fe_2VAl, due to hybridization effects. The pseudogap formation arises from an indirect band overlap at the Fermi energy (E_f), and thus Fe_2VAl is characterized as a semimetal. Results of nuclear magnetic resonance (NMR) (Ref. 19) are in good agreement with these calculations. An optical conductivity measurement on Fe_2VAl further confirmed the existence of a pseudogap at the Fermi level.[20] Band-structure calculations also indicated Fe_2VGa to be a semimetal,[17,21] and a recent NMR study on this material has revealed a small Fermi-level DOS within the pseudogap,[22] consistent with semimetallic characteristics. Moreover, low-temperature specific-heat measurements on Fe_2VAl and Fe_2VGa revealed a huge effective-mass enhancement,[12,23,24] as compared to the values predicted by band-structure calculations. In general, semimetals with heavy band mass are expected to have large Seebeck coefficients.

Upon substituting V onto Fe sites, slightly off the stoichiometric composition, results in a dramatic growth on the low-temperature resistivity.[12–14] This observation suggests that both $Fe_{2-x}V_{1+x}Al$ and $Fe_{2-x}V_{1+x}Ga$ systems for $x>0$ contain fewer carriers. In this investigation, we thus perform a systematic study of the thermoelectric properties including electrical resistivity (ρ), Seebeck coefficient (S), as well as thermal conductivity (κ) on $Fe_{2-x}V_{1+x}Al$ and $Fe_{2-x}V_{1+x}Ga$ between 10 and 300 K. These measurements allow us to examine the thermoelectric properties of these semimetallic Heusler compounds in detail.

II. EXPERIMENTAL DETAILS AND RESULTS

The samples studied here were prepared by mixing appropriate amounts of elemental metals. Briefly, mixture of high-purity elements were placed in a water-cooled copper crucible and then melted several times in an Ar arc-melting furnace. For $Fe_{2-x}V_{1+x}Al$, resulting ingots were annealed in a vacuum-sealed (10^{-5} torr) quartz tube at 1000 °C for 2 days, and then further annealed at 400 °C for more than 12 h; this was followed by furnace cooling. The $Fe_{2-x}V_{1+x}Ga$

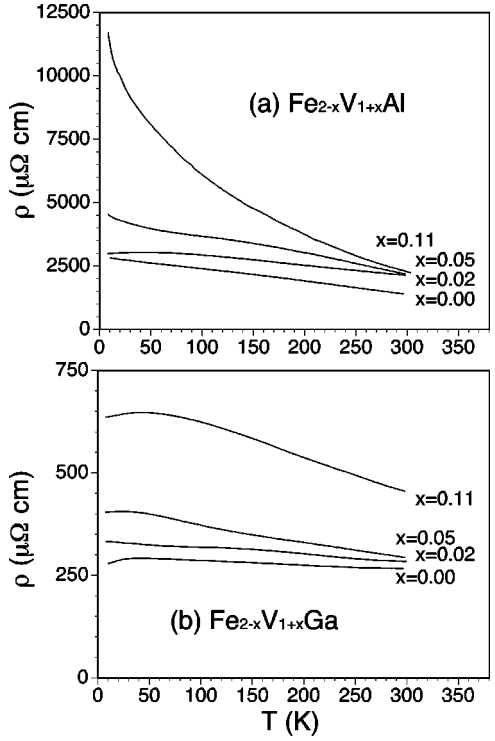

FIG. 1. Electrical resistivity as a function of temperature for $Fe_{2-x}V_{1+x}Al$ and $Fe_{2-x}V_{1+x}Ga$.

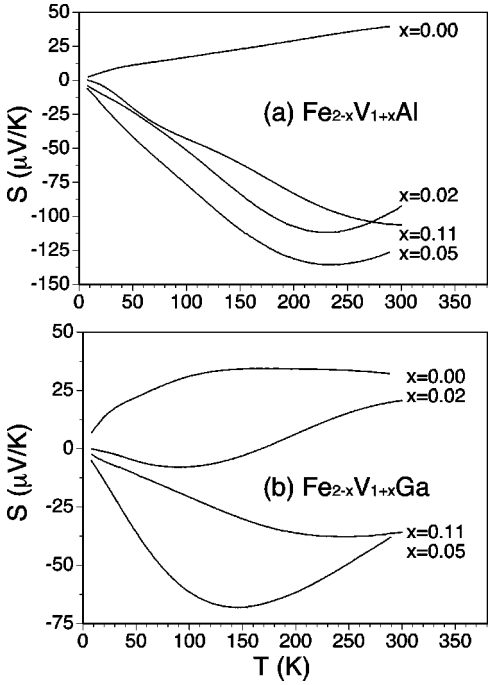

FIG. 2. Seebeck coefficient vs temperature in $Fe_{2-x}V_{1+x}Al$ and $Fe_{2-x}V_{1+x}Ga$.

compounds were annealed at 600 °C and then 400 °C. The same preparation technique has been used in other studies of these materials,[12,23,25,26] which is known to form in a single-phase $L2_1$ (Heusler-type) structure. A Cu $K\alpha$ x-ray analysis on powdered samples from the annealed ingot was consistent with the expected $L2_1$ structure, with no other phases present in the spectrum.

A. Electrical resistivity

The resistivity data were obtained by a standard dc four-terminal method. In Fig. 1 we show the temperature variation of electrical resistivity for $Fe_{2-x}V_{1+x}Al$ and $Fe_{2-x}V_{1+x}Ga$ measured during the warming process. We found that an increasing vanadium substitution causes a drastic growth on the resistivity for both systems, and these materials become more semiconductinglike, consistent with previously reported results.[12,13] Such a substitution effect can be understood by a reduction of the band overlap. Besides, the $Fe_{2-x}V_{1+x}Al$ alloys consistently exhibit higher resistivity compared to $Fe_{2-x}V_{1+x}Ga$, indicating fewer charge carriers in the $Fe_{2-x}V_{1+x}Al$ system. This observation is in good agreement with the results of NMR and band-structure calculations.

B. Seebeck coefficient

Seebeck voltages were detected using a pair of thin Cu wires electrically connected to the sample with silver paint at the same positions as the junctions of differential thermocouple. The stray thermal emfs are eliminated by applying long current pulses ($\sim$100 s) to a chip resistor which serves a heater, where the pulses appear in an off-on-off sequence.

The *T*-dependent Seebeck coefficient of $Fe_{2-x}V_{1+x}Al$ and $Fe_{2-x}V_{1+x}Ga$ is plotted in Fig. 2. The positive values of Seebeck coefficient for the stoichiometric compounds of Fe_2VAl and Fe_2VGa indicate that hole-type carriers dominate the heat transport. In Fe_2VAl, *S* increases with temperature following a quasilinear behavior up to 300 K. On the other hand, the *T*-dependent *S* of Fe_2VGa exhibits a broad maximum near 120 K, and then turns to a negative slope at high temperatures. The downturn of *S* in Fe_2VGa at high temperatures is attributed to the contribution of thermally excited carriers across the energy gap. In fact, the values of energy splitting of 138 meV for Fe_2VAl (Ref. 18) and 110 meV for Fe_2VGa (Ref. 27) have been extracted from the NMR spin-lattice relaxation rates. Thus our results of Seebeck coefficient on Fe_2VAl and Fe_2VGa are reasonably consistent with the NMR measurements. For Fe_2VAl, the splitting energy is relatively large, and such a thermally activated response is expected to occur at higher temperatures, indeed observed by Nishino *et al.*[27]

For the nonstoichiometric samples, the sign of *S* changes to negative values in the $Fe_{2-x}V_{1+x}Al$ system upon V substitution, indicating a change of conduction mechanism or dominant carrier in these compounds. The absolute value of *S* increases initially with *x*, but tends to decrease with more V substitution onto Fe sites ($x=0.11$). Broad minimums in *S* appear at around 220 and 240 K for $x=0.02$ and $x=0.05$, respectively. The *S* minimum for $x=0.11$ has not yet reached up to 300 K, but the trend of flattening out on *S* at high temperature is clearly seen in Fig. 2(a). The upturn in *S* at high temperatures could be ascribed to the thermally excited positive carriers across the energy gap, and the width of gap

in these alloys becomes narrower with increasing x. Such an observation is in good agreement with the results of NMR for $Fe_{2-x}V_{1+x}Al$; the values of energy splitting of about 138 meV for Fe_2VAl ($x=0$) and 48 meV for $Fe_{1.95}V_{1.05}Al$ ($x=0.05$) were reported.[28] The maximum absolute value of S as large as 130 μV/K (a factor of 5 larger than $x=0$) at around 240 K was observed in $Fe_{1.95}V_{1.05}Al$, suggesting indeed a promising candidate for potential thermoelectric applications in this system. For $Fe_{2-x}V_{1+x}Ga$, the T-dependent S exhibits similar behavior as in $Fe_{2-x}V_{1+x}Al$, but the upturns in S take place at lower temperatures. This provides an indication of narrower energy gaps in the $Fe_{2-x}V_{1+x}Ga$ system. Interestingly, the $Fe_{1.98}V_{1.02}Ga$ compound shows negative values of Seebeck coefficient at low temperatures and then changes to positive values at high temperatures, crossing zero at around 170 K. The small absolute value of S (less than 10 μV/K below 240 K) implies that the electrons and holes involved in the heat transport processes are ''nearly compensated.'' However, in the high-temperature regime the holes are dominate and thus contribute the positive Seebeck voltage. For all $Fe_{2-x}V_{1+x}Ga$ alloys we investigated, the largest absolute value of $S \sim 70$ μV/K was found in $Fe_{1.95}V_{1.05}Ga$ near 140 K.

C. Thermal conductivity

To further evaluate the possibility for potential thermoelectric applications in these materials, we performed thermal-conductivity (κ) measurements between 10 and 300 K. Thermal-conductivity measurements were carried out in a close-cycle refrigerator, using a direct heat-pulse technique. Samples were cut to a rectangular parallelepiped shape of typical size of $1.5\times1.5\times5.0$ mm^3 with one end glued (with thermal epoxy) to a copper block that served as a heat sink, while a calibrated chip resistor as a heat source glued to the other end. The temperature difference was controlled to be less than 1 K to minimize the heat loss through radiation. The temperature difference was measured by using an E-type differential thermocouple with junctions thermally attached to two well-separated positions along the sample.

In Fig. 3, we display the observed thermal conductivity for all studied samples. At low temperatures, κ increases with temperature and a maximum appears between 40 and 60 K, close to that reported for the half-Heusler compounds.[2,7,10] This is a typical feature for the reduction of thermal scattering at lower temperatures. The maximum takes place at the temperature where the phonon mean-free-path is approximately equal to the crystal site distance. After passing through the maximum, κ drops with increasing temperature, tending to vary with $1/T$. An obvious trend found in these measurements is that κ decreases with increasing x. The reduction of heat conduction with substitution can be easily understood by a shorter phonon mean-free-path due to impurities or defects scattering. The total thermal conductivity can be expressed as a sum of lattice and electronic terms. The lattice part is expected to follow $1/T$ behavior, as we did observe here. Since the electronic contribution to κ for all studied compounds is small, the measured thermal conductivity shown in Fig. 3 is essentially the lattice thermal conductivity. The values of κ at room temperature are rather large for all samples we studied: 20–25 W/mK for $Fe_{2-x}V_{1+x}Al$ and 14–18 W/mK for $Fe_{2-x}V_{1+x}Ga$, approximately one order of magnitude higher than those in the well-known thermoelectric materials ($\kappa\sim1.6$ W/mK in Bi_2Te_3).

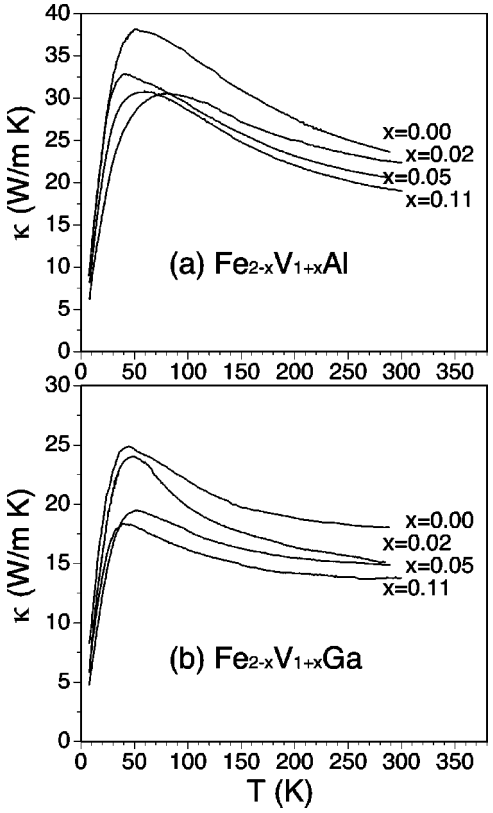

FIG. 3. Temperature dependence of the thermal conductivity in $Fe_{2-x}V_{1+x}Al$ and $Fe_{2-x}V_{1+x}Ga$.

III. DISCUSSION

It is known that the Seebeck coefficient measurement is a sensitive tool of probing the energy relative to the Fermi surface and the results could yield information about the Fermi-level band structure. According to the band-structure calculations on Fe_2VAl by Weht and Pickett,[17] about 42% of the electronic states at Fermi level arise from V-dominated electron pockets, with the others from Fe-dominated hole pockets. The positive S value for Fe_2VAl indicates that the hole carriers are heavier and thus dominate the heat transport. Our result of Seebeck coefficient measurement on Fe_2VAl is consistent with the theoretical predication, and in excellent agreement with the result of Hall-effect measurements.[29,30] We believe that such an argument is also appropriate to the isostructure compound Fe_2VGa.

Now, we discuss the off-stoichiometric effect on the Seebeck coefficient and Fermi-level band structure. Since the electron pockets arise from the V $3d$ bands, substitution of V onto Fe sites would result in an increase of electronic carriers but a reduction of hole carriers. However, such a change could not be simply described by a rigid-band model, which only shifts E_f to a higher energy. By using the calculated

electron and hole effective masses of $Fe_{2-x}V_{1+x}Al$,[17] one finds that the Fermi energy of $Fe_{1.95}V_{1.05}Al$ shifted well outside the pseudogap. This prediction gives a significantly larger change in DOS at the Fermi level than what were observed experimentally. A more realistic approach is provided by a recent Korringa-Kohn-Rostoker coherent potential approximation (KKR-CPA) calculation for $Fe_{2-x}V_{1+x}Al$ and $Fe_{2-x}V_{1+x}Ga$.[21] Rather than filling states near E_f, the effect of excess vanadium to stoichiometric Fe_2VAl and Fe_2VGa is to enhance the low-lying V-dominated states. As a result, E_f moves up relative to the pseudogap. In addition, a simple rigid band picture could not explain the decrease of S value with a higher level of V substitution ($x=0.11$). In these compositions ($Fe_{1.89}V_{1.11}Al$ and $Fe_{1.89}V_{1.11}Ga$), the shift of E_f and band-edge modification both play important roles to reduce their effective masses and electron-hole symmetry, and thus reduce the S values.

It is worthwhile comparing our results with those found in the $(Fe_{2/3}V_{1/3})_{100-y}Al_y$ system.[27] In that study a small deviation of Al content from the stoichiometric composition ($y=25$) causes a decrease in the low-temperature resistivity and a significant increase in the Seebeck coefficient. Such a result is quite different from that observed in our present study of $Fe_{2-x}V_{1+x}Al$. Based on the band-structure calculations for Fe_2VAl,[15–18] either a slight increase or decrease of Al content would give rise to an increase of total density of states, which in turn leads to a reduction of the low-temperature resistivity in $(Fe_{2/3}V_{1/3})_{100-y}Al_y$. From the application viewpoint, the efficiency of a thermoelectric material is given by the dimensionless parameter figure-of-merit $ZT=S^2T/\rho\kappa$. Accordingly, it would be reasonable to predict that the $(Fe_{2/3}V_{1/3})_{100-y}Al_y$ system is an intriguing candidate for low- and intermediate-temperature thermoelectric applications. For the present studied systems, although the low-level V substitution has a significant enhancement on the Seebeck coefficient (S), the ZT values of these materials are still small. This is mainly due to the fact that the resistivity (ρ) increases drastically but the reduction of their large values of thermal conductivity (κ) is marginal with such a substitution. The largest ZT value found among the studied compositions is only about 0.03 (for $Fe_{1.95}V_{1.05}Ga$ at around 140 K), an order of magnitude smaller than conventional thermoelectric materials such as Bi_2Ti_3.

IV. CONCLUSIONS

In conclusion, a full investigation of the thermoelectric properties of the stoichiometric and off-stoichiometric Heusler compounds $Fe_{2-x}V_{1+x}M$ ($M=$ Al, Ga) for $x\geqslant 0$ was performed. Seebeck coefficients are positive for the stoichiometric compounds Fe_2VAl and Fe_2VGa, signifying that hole-type carriers dominate the heat transport. Upon V substitution, a significant enhancement accompanied by the sign change in S in both systems are observed. Such an effect can be attributed to the shift of Fermi energy E_f and the modification of electron and hole pockets near band edges. The observed upturns in S at high temperatures are presumably due to the contribution of thermally excited quasiparticles across their energy gaps. These observations are consistent with previously reported experimental results and theoretical band-structure calculations. Although the nonstoichiometric alloys do exhibit much larger Seebeck coefficients, their high values of resistivity and thermal conductivity make them rather poor thermoelectric materials. Apparently, the thermoelectric properties in these ternary semimetallic compounds have not been optimized and warrant further investigation.

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[1] B.C. Sales, D. Mandrus, and R.K. Williams, Science **272**, 1325 (1996).
[2] H. Hohl, A.P. Ramirez, C. Goldmann, G. Ernst, B. Woelfing, and E. Bucher, J. Phys.: Condens. Matter **11**, 1697 (1999).
[3] F.G. Aliev, N.B. Brandt, V.V. Moshchalkov, V.V. Kozyrkov, R.V. Skolozdra, and A.I. Belogorokhov, Z. Phys. B: Condens. Matter **75**, 167 (1989).
[4] F.G. Aliev, V.V. Kozyrkov, V.V. Moshchalkov, R.V. Skolozdra, and K. Durczewski, Z. Phys. B: Condens. Matter **80**, 353 (1990).
[5] F.G. Aliev, Physica B **171**, 199 (1991).
[6] H. Hohl, A.P. Ramirez, C. Goldmann, G. Ernst, B. Woelfing, and E. Bucher, J. Phys.: Condens. Matter **10**, 7843 (1998).
[7] C. Uher, J. Yang, S. Hu, D.T. Morelli, and G.P. Meisner, Phys. Rev. B **59**, 8615 (1999).
[8] K. Mastronardi, D. Young, C.C. Wang, P. Khalifah, R.J. Cava, and A.P. Ramirez, Appl. Phys. Lett. **74**, 1415 (1999).
[9] P. Larson, S.D. Mahanti, S. Sportouch, and M.G. Kanatzidis, Phys. Rev. B **59**, 15 660 (1999).
[10] D.P. Young, P. Khalifah, R.J. Cava, and A.P. Ramirez, J. Appl. Phys. **87**, 317 (2000).
[11] Y. Xia, V. Ponnambalam, S. Bhattacharya, A.L. Pope, S.J. Poon, and T.M. Tritt, J. Phys.: Condens. Matter **13**, 77 (2001).
[12] Y. Nishino, M. Kato, S. Asano, K. Soda, M. Hayasaki, and U. Mizutani, Phys. Rev. Lett. **79**, 1909 (1997).
[13] K. Endo, H. Matsuda, K. Ooiwa, M. Iijima, K. Ito, T. Goto, and A. Ono, J. Phys. Soc. Jpn. **66**, 1257 (1997).
[14] N. Kawamiya, Y. Nishino, M. Matsuo, and S. Asano, Phys. Rev. B **44**, 12 406 (1991).
[15] G.Y. Guo, G.A. Botton, and Y. Nishino, J. Phys.: Condens. Matter **10**, L119 (1998).
[16] D.J. Singh and I.I. Mazin, Phys. Rev. B **57**, 14 352 (1998).
[17] R. Weht and W.E. Pickett, Phys. Rev. B **58**, 6855 (1998).
[18] M. Weinert and R.E. Watson, Phys. Rev. B **58**, 9732 (1998).
[19] C.S. Lue and J.H. Ross, Jr., Phys. Rev. B **58**, 9763 (1998).
[20] H. Okamura, J. Kawahara, T. Nanba, S. Kimura, K. Soda, U. Mizutani, Y. Nishino, M. Kato, I. Shimoyama, H. Miura, K. Fukui, K. Nakagawa, H. Nakagawa, and T. Kinoshita, Phys. Rev. Lett. **84**, 3674 (2000).

[21] A. Bansil, S. Kaprzyk, P.E. Mijnarends, and J. Tobola, Phys. Rev. B **60**, 13 396 (1999).
[22] C.S. Lue and J.H. Ross, Jr., Phys. Rev. B **63**, 054420 (2001).
[23] K. Endo, H. Matsuda, K. Ooiwa, M. Iijima, T. Goto, K. Sato, and I. Umehara, J. Magn. Magn. Mater. **177-181**, 1437 (1998).
[24] C.S. Lue, J.H. Ross, Jr., C.F. Chang, and H.D. Yang, Phys. Rev. B **60**, R13 941 (1999).
[25] C.S. Lue, J.H. Ross, Jr., K.D.D. Rathnayaka, D.G. Naugle, S.Y. Wu, and W.-H. Li, J. Phys.: Condens. Matter **13**, 1585 (2001).
[26] I. Maksimov, D. Baabe, H.H. Klauss, F.J. Litterst, R. Feyerherm, D.M. Tobbens, A. Matsushita, and S. Sullow, J. Phys.: Condens. Matter **13**, 5487 (2001).
[27] Y. Nishino, H. Kato, M. Kato, and U. Mizutani, Phys. Rev. B **63**, 233303 (2001).
[28] C.S. Lue and J.H. Ross, Jr., Phys. Rev. B **61**, 9863 (2000).
[29] M. Kato, Y. Nishino, S. Asano, and S. Ohara, J. Jpn. Inst. Met. **62**, 669 (1998).
[30] A. Matsushita, T. Naka, Y. Takano, T. Takeuchi, T. Shishido, and Y. Mamada, Phys. Rev. B **65**, 075204 (2002).