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MAGNETISM AND FERROELECTRICITY

Magnetic and Electrical Properties of the $ZnGeAs_2$: Mn Chalcopyrite

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Abstract—Doping of the $ZnGeAs_2$ semiconductor with manganese has produced compositions with spontaneous magnetization and high Curie temperatures of up to 367 K for the composition 3.5 wt. % Mn. Their magnetic properties are characteristic of spin glasses at temperatures $T < T_S$ and magnetic fields $H < 11$ kOe. In stronger fields, the spin glass state transforms into a phase with a spontaneous magnetization 20–30 times weaker than that to be expected under ferromagnetic ordering of all Mn ions. This is obviously a singly-connected ferromagnetic phase containing regions with frustrated bonds. The frustrated regions and the spin glass phase have inclusions of noninteracting ferromagnetic clusters, because these regions and the spin glass phase at low temperatures exhibit a strong increase in the magnetization M, with the dependence $M(T)$ being described by the Langevin function. Measurements of the electrical resistivity ρ and the Hall effect have revealed that, for $T < 30$ K, the resistivity ρ of compositions with 1.5 and 3.5 wt. % Mn is higher that at 30 K, which makes superexchange dominant and gives rise to the onset of the spin glass state. The nonuniform distribution of Mn ions in the spin glass phase accounts for the existence of isolated ferromagnetic clusters, their ferromagnetism being generated by carrier-mediated exchange. As the temperature increases still more, the increase in the mobility occurs faster than the decrease in the concentration, thus promoting an enhancement of the carrier-mediated exchange and growth of the ferromagnetic clusters in size, which at $T = T_S$ come in contact. This signifies a transition from a multiply- to a singly-connected ferromagnetic phase, which contains microregions with frustrated bonds.

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1. INTRODUCTION

The early 1990s have witnessed emergence of a new area in the physics of solid state based on the possibility of transfer of an oriented electron spin from a ferromagnet to a nonmagnetic semiconductor [1, 2]. Part of this research having an application potential was named spintronics. These studies are of considerable importance for development of one-electron logical structures and spin-information systems in informatics (in this particular case, spin-based informatics, in which the electron spin serves as the information storage cell, with one spin providing one bit of information [3]). In solid-state electronics, spin current transport opens up a novel possibility of using magnetic field to control the characteristics of various devices, diodes, triodes etc.; i.e., it provides an additional degree of freedom. Ferromagnetic metals used as emitters of polarized spins are capable of providing a spin polarization degree of not above 10%. A substantially higher polarization degree (of up to 100%) was obtained in semiconductor–EuO and semiconductor–chalcogenide-spinel structures, but only at cryogenic temperatures, an aspect unfavorable for applications. Besides, one is plagued in this case by a technological difficulty, more specifically, that of achieving a good electrical contact between a ferromagnet and a semiconductor.

A good electrical contact and a high spin-polarized current can be reached by developing an ferromagnetic semiconductor with a Curie point above room temperature through doping with impurities with incompletely filled 3*d* shells. This is why interest of researchers became focused on development of ferromagnetic semiconductors through doping semiconductors customarily employed in microelectronics, primarily the III–V compounds, with manganese. The best studied representative of this class of materials is $Ga_{1-x}Mn_xAs$ which revealed ferromagnetism with a Curie temperature T_C not in excess of 170 K [4, 5].

High-temperature ferromagnetism has been recently observed in Mn-doped II–IV–V_2 chalcopyrites. These were $CdGdP_2$: Mn [6], $ZnGeP_2$: Mn [7],

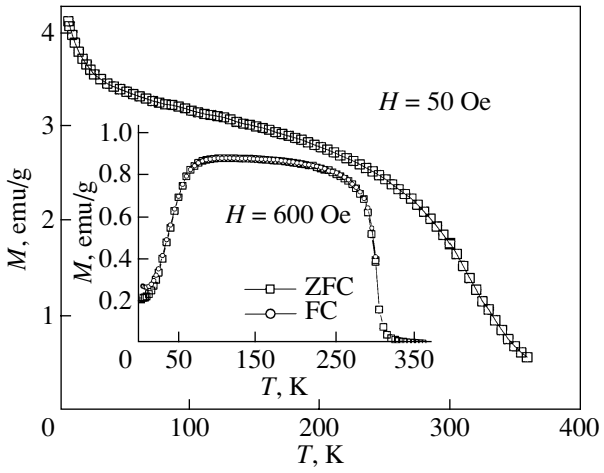

Fig. 1. Temperature dependence of the magnetization M for the composition $ZnGeAs_2$ with 3.5 wt. % Mn in magnetic fields of 50 kOe and 0.6 kOe (inset). The ZFC curve: the sample was zero-field-cooled from 400 to 5 K, after which its magnetization was measured under heating. The FC curve: the sample was cooled in a field of 0.6 kOe from 400 to 5 K with parallel measurement of its magnetization.

and $ZnSnAs_2$: Mn [8], compounds with the Curie point as high as 350 K. We reported on the compound $CdGeAs_2$: Mn, whose Curie temperature T_C was still higher, 355 K.

The II–IV–V_2 ternary semiconductors have been known for a long time. These compounds are crystallochemical and electronic analogs of the III–V semiconductors. Interest in these compounds emerged after one discovered their unique nonlinear optical properties, namely, the high nonlinear polarizability and birefringence, which opened a way to their use for parametric conversion of laser radiation in the mid-IR range. The most promising for this purpose are high-purity $CdGeP_2$, $CdGeAs_2$, and $ZnGeP_2$ crystals. The II–IV–V_2-type compounds retain the main features characteristic of the III-V materials, namely, the predominantly covalent bonding, small effective carrier masses, relatively high mobilities of the electrons and holes, and persistence of the absolute minima and maxima of the conduction and the valence band at Brillouin zone center.

We prepared and studied new $ZnGeAs_2$: Mn compounds with the Curie point reaching 367 K, a record-high value for II–IV–V_2-type compounds. The $ZnGeAs_2$ compound studied in the present work possesses the following characteristics: bandgap 0.85 eV; mobility ~10^2 cm^2/V s (for holes with concentrations of 10^{18}–5×10^{19} cm^{-3}); effective hole mass 0.4–0.74. This makes the II–IV–V_2 : Mn compounds promising for spintronics applications.

2. EXPERIMENTAL TECHNIQUE

We report here on a study of the magnetization, electrical resistivity ρ, magnetoresistance $\Delta\rho/\rho = (\rho_H - \rho_{H=0})/\rho_{H=0}$ and the Hall effect of polycrystalline $ZnGeAs_2$: Mn samples with Mn contents of 1.5 to 3.5 wt. %. The magnetization was measured with a SQUID magnetometer. The four-probe technique was employed to measure ρ and Δρ/ρ. The Hall effect was studied by the standard dc method. The contacts to the samples were secured with current-conducting glue.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The $ZnGeAs_2$ samples were prepared by direct alloying of high-purity powders of $ZnAs_2$ and Ge taken in stoichiometric ratio. Mn was introduced according to the hypothetical $ZnGeAs_2$–$MnGeAs_2$ cut. To increase the Mn solubility, the rate of cooling from 900°C was chosen not lower than 5–10 K/s. X-ray diffraction analysis showed all samples with the Mn contents of 1.5, 3, and 3.5 wt. % to be single phase, thus identifying them as $ZnGeAs_2$. A comparison of the lattice constants revealed that the cell volume decreases with increasing Mn content, which suggests formation of solid solutions through Mn substitution for Zn. The contents of the components were checked by x-ray fluorescence. A study of the distribution of elements over the sample length showed that Zn : Ge : As = 1 : 1 : 2. Within experimental error, the Mn was found to be distributed uniformly over the sample length.

Figure 1 displays temperature dependence of the magnetization, $M(T)$, for the composition with 3.5 wt. % Mn in a magnetic field H = 50 kOe. The $M(T)$ curve obtained for $T > 60$ K is seen to be characteristic of a ferromagnet. For $T < 60$ K, however, magnetization is observed to grow strongly with decreasing temperature, an effect that can be interpreted as an additional contribution due to the superparamagnetic phase. The inset to Fig. 1 shows the $M(T)$ plot measured in a weak magnetic field of 600 Oe. The $M(T)$ curves obtained in a strong (50 kOe) and a weak (0.6 kOe) field are immediately seen to differ substantially. When measuring in the weak field, the magnetization is observed to drop strongly as the temperature falls below T_S = 86 K, with M decreasing 4.5 times. At T_k = 10 K, this drop stops, and here one sees a difference between the magnetizations of the sample cooled from $T > T_C$ in this weak magnetic field (FC curve) and the one that was zero-field cooled (ZFC curve) The FC curve exhibits a rise with further decrease in the temperature. Shown in Fig. 2 are $M(T)$ curves in the temperature interval including T_S, which were measured in magnetic fields of 3, 6, 8, 9, and 11 kOe. Examining this figure shows that as H increases, the decrease in the magnetization at $T = T_S$ becomes weaker to disappear altogether at 11 kOe, and the value of T_S shifts toward lower temper-

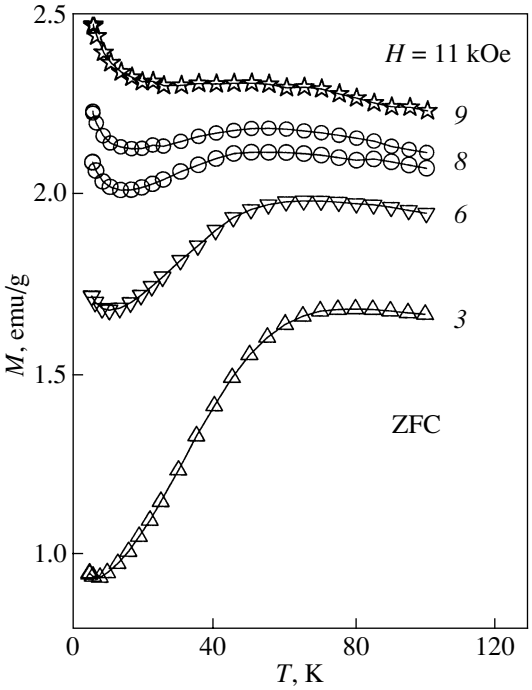

Fig. 2. Temperature dependence of the magnetization M for the composition $ZnGeAs_2$ with 3.5 wt. % Mn in different magnetic fields in the temperature range from 5 to 100 K. Each curve was measured after the sample had been cooled to 5 K with no magnetic field.

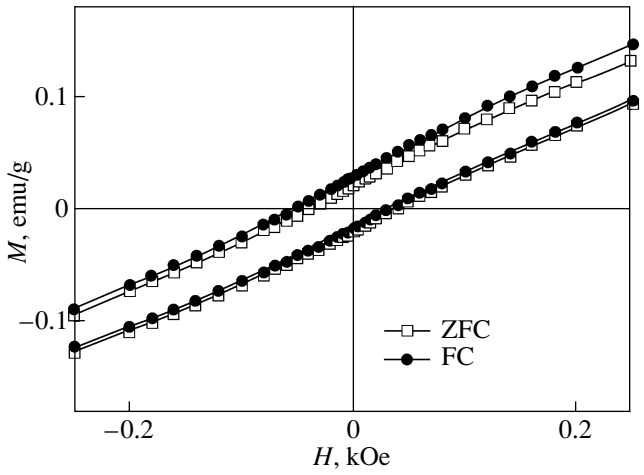

Fig. 3. Central part of the hysteresis loop of $ZnGeAs_2$ sample with 3.5 wt. % Mn, which was measured at 5 K in a magnetic field from +0.6 to –0.6 kOe. We readily see the loop for the sample cooled to 5 K in a magnetic field of 0.6 kOe to shift along the H axis, whereas the loop measured in zero field is symmetric.

atures. Indeed, as the field increases from 600 Oe to 9 kOe, T_S decreases from 86 to 49 K. This is paralleled by the rise in the $M(T)$ curves observed to occur for $T < T_k$ becoming ever stronger manifest with increasing H. Figure 3 displays hysteresis curves measured on the FC and ZFC samples at 5 K. We see the loop of the FC sample to shift along the H axis. The other compositions of this system revealed a similar behavior of the magnetization, with the above features becoming ever less pronounced as the manganese content decreased.

This behavior of the magnetization suggests a transition at $T = T_S$ from a state with spontaneous magnetization to the spin glass state (SG), i.e., a behavior inverse to the spin glass state. This spin glass contains noninteracting magnetic clusters, because the $M(T)$ relation for $T < T_k$ obeys the Langevin relation. The process observed to occur at $T = T_S$ cannot be a ferromagnet–antiferromagnet transition, because it vanishes in a relatively weak field, and the value of T_S itself depends on magnetic field. Besides, as evident from Fig, 4, for $T < T_S$ the $M(H)$ relation remains nonlinear up to the maximum fields available, 50 kOe; if for $T < T_S$ the sample had been antiferromagnetic, this relation would have been linear.

It appeared of interest to find what is the spontaneous magnetization phase existing for $T < T_S$. In the above-mentioned references [4–9], the phase with spontaneous magnetization observed in Mn-doped dilute magnetic semiconductors of the II–IV–V_2 and III-V types was referred to as "ferromagnetic", although the magnetic moment per Mn ion at helium temperatures measured in them experimentally was substantially lower than the limiting value of $5\mu_B$. The magnetic moment per Mn ion (μ_s) in the $ZnGeAs_2$ composition with 3.5 wt. % Mn, whose magnetic properties were described above, was found to be ~$1\mu_B$. This value was derived from the magnetization M_S which was obtained by extrapolation of close to rectilinear part of the $M(T)$ curve, measured at 50 kOe, to the M axis. This value of μ_s is 4–5 times smaller than magnetic moments of the Mn^{3+} and Mn^{2+} ions, an observation that suggests that the larger part of the volume of this "ferromagnetic" phase is in actual fact occupied by regions with frustrated bonds. Approximately the same values of μ_s were obtained for other compositions of the system under study as well. This suggests that the magnetization behaves in a complex way up to the maximum field reached (50 kOe). For $T < T_S$ and $H \le 9$ kOe, the spin glass state persists; in still stronger fields it is replaced by a singly connected ferromagnetic phase containing embedded regions with frustrated bonds. The frustrated regions contain noninteracting superparamagnetic clusters. This makes the concept of the Curie temperature for such a system fairly conventional; indeed, it is the Curie temperature of the singly connected ferromagnetic phase. It cannot be determined by the method of Belov–Arrott thermodynamic coefficients because of the system being magnetically nonuniform. As ambiguous would be determination of T_C from magnetization in weak magnetic fields, because this magnetization is connected intimately with the demagnetizing factor. The demagnetizing factor of the singly connected fer-

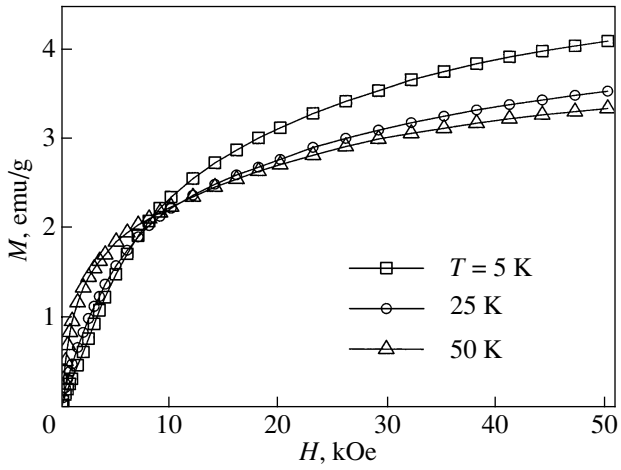

Fig. 4. Magnetization isotherms of the $ZnGeAs_2$ sample with 3.5 wt. % Mn at different temperatures. Each curve was measured after the sample had been cooled to 5 K in a zero magnetic field.

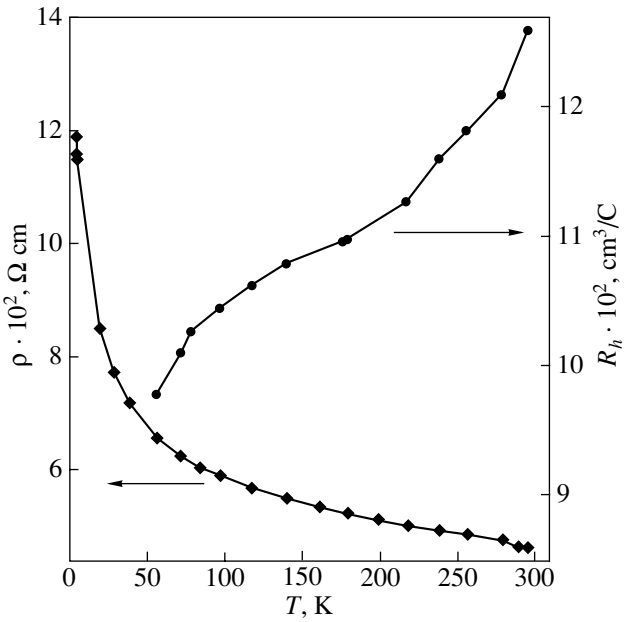

Fig. 5. Temperature dependence of the electrical resistivity ρ and the normal Hall coefficient R_H for the $ZnGeAs_2$ sample with 1.5 wt. % Mn.

romagnetic phase depends on its configuration, which varies with temperature. Therefore, for the Curie point was taken the temperature obtained by extrapolation of the steepest part of the $M(T)$ curve measured in the maximum field reachable (50 kOe) to its intercept with the temperature axis. The Curie temperature was found to be 367 K. This is the highest Curie temperature found thus far in the II–IV–V_2 : Mn systems. This provided substantiation for the theoretical suggestion [10] that the Curie temperatures of Zn-containing chalcopyrites should be higher than those of the corresponding Cd-based ones.

The Hall electric field of the samples under study was found to depend linearly on magnetic field, which evidences the absence of anomalous Hall effect. Measurements of the electrical resistivity and of the Hall effect revealed that all the samples support hole conduction, with the hole concentration $p \sim 10^{19}$–10^{20} cm^{-3} and mobility varying from 0.25 to 2.5 cm^2 V^{-1} s^{-1}. Figures 5 and 6 plot the temperature dependences of the electrical resistivity ρ, normal Hall coefficient R_H and mobility. We readily see that the $\rho(T)$ relation of the 1.5 wt. % Mn composition follows a pattern characteristic of semiconductors, while the $p(T)$ curve has a purely metallic signature, with p varying very little, from 6.4×10^{19} cm^{-3} at $T = 50$ K to 5.2×10^{19} cm^{-3} at 300 K. The mobility grows faster, from 1.25 cm^2 V^{-1} s^{-1} at 20 K to 2.6 cm^2 V^{-1} s^{-1} at 300 K. In the 3.5 wt. % Mn composition, $\rho(T)$ passes through a minimum at $T \sim$ 30 K, and the mobility increases by an order of magnitude in the region $10 \le T \le 300$ K, whereas p varies from 2.5×10^{20} cm^{-3} at 50 K to 8×10^{19} cm^{-3} at 300 K. The magnetoresistance is small; it does not exceed 4% at $H = 8$ kOe.

The origin of ferromagnetism in dilute magnetic semiconductors was studied by first-principles electronic structure calculations [11, 12]. It is maintained [11, 12] that the effective exchange interaction in these compounds derives primarily from competition between double exchange and superexchange interactions. It is known that semiconductors with chalcopyrite structure are stabilized by internal defects acting as sources of holes which form stable complexes with Mn

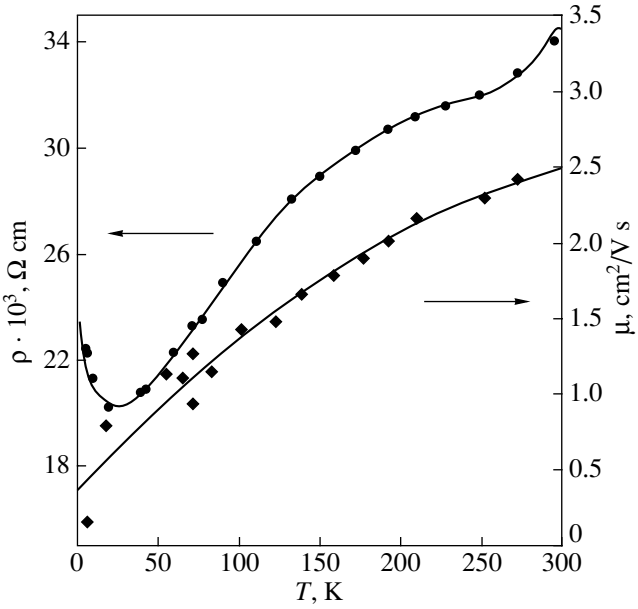

Fig. 6. Temperature dependence of the electrical resistivity ρ and the hole mobility for the $ZnGeAs_2$ sample with 3.5 wt. % Mn.

[13]. It should be pointed out that double exchange involves carrier transfer among ions residing in different valence states, in this particular case, between Mn^{2+} and Mn^{3+}. As shown earlier, in the system under study Mn substitutes for Zn, so that the above complexes are actually (Zn, V_C, Mn), where V_C are vacancies. It is not known, however, how vacancies affect the distribution of the Mn^{2+} and Mn^{3+} ions. Therefore we are going to replace subsequently the term "double exchange" with a broader concept of "carrier-mediated exchange". As seen from Figs. 5 and 6, for $T < 30$ K, the electrical resistivity of the compositions with 1.5 and 3.5 wt. % Mn is higher than that at 30 K, a factor that apparently accounts for the superexchange becoming dominant. As shown in [14], spin glass is the ground state in this case. As the temperature increases, mobility increases with a rate faster than that of the small concentration drop, thus favoring carrier-mediated exchange, which initiates the transition from the spin glass to the ferromagnetic state. One could suggest also another scenario based on the energies of superexchange and carrier-mediated exchange being close, which is not in conflict with the observed magnetic and transport properties. Because the Mn ions dissolving in $ZnGeAs_2$ become randomly distributed, one may conceive formation at low temperatures in the spin glass matrix of ferromagnetic clusters, whose ferromagnetism rests upon the higher carrier-mediated exchange energy. As the temperature increases, these clusters grow in volume due to the increasing hole mobility, until at a certain temperature these clusters come in contact. This signals the transition from a multiply connected ferromagnetic phase made up of isolated ferromagnetic clusters to the singly connected ferromagnetic phase, within which microregions with frustrated bonds are embedded.

REFERENCES

1. H. Ohno, Science (Washington) **281**, 951 (1998).
2. G. A. Prinz, Science (Washington) **282**, 1660 (1998).
3. F. Matsukura, H. Ohno, A. Shen, and Y. Sugawara, Phys. Rev. B: Condens. Matter **57**, R2037 (1998).
4. K. M. Edmonds, K. Y. Wang, R. P. Campion, A. C. Neumann, N. R. S. Farley, B. L. Gallagher, and C. T. Foxon, Appl. Phys. Lett. **81**, 4991 (2002).
5. K. M. Edmonds, P. Boguslawski, K. Y. Wang, R. P. Campion, S. N. Novikov, N. R. S. Farley, B. L. Gallagher, C. T. Foxon, M. Sawicki, T. Dietl, M. Buongiorno Nardelli, and J. Bernholc, Phys. Rev. Lett. **92**, 03720 (2004).
6. G. A. Medvedkin, T. Ishibashi, T. Nishi, K. Hayata, Y. Hasegawa, and K. Sato, Jpn. J. Appl. Phys. **39**, L949 (2000).
7. G. A. Medvedkin, K. Hirose, T. Ishibashi, T. Nishi, V. G. Voevodin, and K. Sato, J. Cryst. Growth **236**, 609 (2002).
8. S. Choi, G.-B. Cha, S. C. Hong, S. Cho, Y. Kim, J. B. Ketterson, S.-Y. Jeong, and G.-C. Yi, Solid State Commun. **122**, 165 (2002).
9. R. V. Demin, L. I. Koroleva, S. F. Marenkin, S. G. Mikhaĭlov, V. M. Novotortsev, V. T. Kalinnikov, T. G. Aminov, R. Szymczak, G. Szymczak, and M. Baran, Pis'ma Zh. Tekh. Fiz. **30** (21), 81 (2004) [Tech. Phys. Lett. **30** (11), 924 (2004)].
10. P. R. Kent and T. C. Schulthess, in *Proceedings of the 27th International Conference on Physics of Semiconductors (ICPS-27), Flagstaff, AZ, 2005*, Ed. by J. Menendez and Ch. G. van de Walle (Flagstaff, 2005), p. 1369.
11. H. Akai, Phys. Rev. Lett. 81, 3002 (1998).
12. H. Akai, T. Kamatani, and S. Watanabe, J. Phys. Soc. Jpn. **69** (Suppl. A), 112 (2000).
13. P. Mahadevan and A. Zunger, Phys. Rev. Lett. **88**, 047205 (2002).
14. Y.-J. Zhao, W. T. Geng, A. J. Freeman, and T. Oguchi, Phys. Rev. B: Condens. Matter **63**, R201202, (2001).

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