

## ***d-d* exchange interactions in narrow-gap diluted magnetic semiconductors: The case of $\text{Hg}_{1-x}\text{Co}_x\text{S}$**

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The magnetic properties of zincblende  $\text{Hg}_{1-x}\text{Co}_x\text{S}$ , where  $x=0.024$  and  $x=0.044$  were investigated. The magnetic susceptibility was measured in the temperature range from 1.8 K to 300 K. The magnetization studies were performed in magnetic fields up to 50 kOe at two temperatures: 1.8 K and 3.0 K. The standard analysis of high-temperature susceptibility gave the value of effective exchange constant  $J_{eff} = -42 \text{ K} \pm 5 \text{ K}$  which implies the nearest-neighbor interaction strength  $J_{NN} = -31 \text{ K} \pm 4 \text{ K}$ . The simultaneous description of the magnetic susceptibility and magnetization data in extended nearest-neighbor pair approximation with the interaction strength  $J_{NN}$  as the only fitting parameter leads to the value  $J_{NN} = -33 \text{ K} + 1/-2 \text{ K}$ . It was also proved that the radial decay of the long-range exchange interaction for more distant neighbors is proportional to  $R^{-5}$ . This finding seems to be an intrinsic characteristic for narrow-gap diluted magnetic semiconductors.

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### I. INTRODUCTION

Diluted magnetic semiconductors (DMS) are mixed crystals in which part of the cation sublattice is randomly substituted by transition-metal ions. The properties of such materials have attracted much scientific interest over the last three decades and many review papers have been devoted to this topic (see, e.g., Refs. 1 and 2). In particular, the magnetic properties of DMS are of special importance because they strongly influence the electrical and optical properties of crystals under consideration. Initially, these studies concentrated on DMS containing Mn because of its high solubility in II-VI compounds. DMS systems containing other transition metals like  $\text{Fe}^{2+}$  or  $\text{Co}^{2+}$  ions have been successfully synthesized later. Magnetic properties of wide-gap semiconductors containing  $\text{Co}^{2+}$  were summarized in several review papers.<sup>3-5</sup>

An interesting problem concerning the nature of the exchange interaction between magnetic ions in narrow-gap II-VI DMS is its particular distance dependence. This exchange is mediated by the virtual electron-hole pair excitations in the energy band and it has a non-Heisenberg form.<sup>6,7</sup> According to theoretical predictions<sup>6,7</sup> the decrease of exchange integrals  $J_i$  with an increasing distance  $R_i$  could be described in such case by the power-law decay in the form  $J_i(R_i) \propto R_i^{-n}$ , where  $i=1,2,3, \dots$  and  $n=5$ . The available experimental data confirm these predictions. However, all these data were taken on Mn-based mixed crystals only (Refs. 8 and 9 for  $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ ,  $\text{Hg}_{1-x}\text{Mn}_x\text{Se}$ , and  $\text{Hg}_{1-x}\text{Mn}_x\text{S}$ , respectively). The question that arises is whether the decay corresponding to  $n=5$  is typical for Mn-based II-VI narrow-gap mixed crystals only or might it be an universal law that is fulfilled for all transition-metal ions embedded in this matrix.

Mercury chalcogenides are an interesting alternative to investigate further the universal validity of  $n=5$  in the

power-law decay describing the radial dependence of the exchange integral in II-VI narrow-gap DMS. Due to the low solubility limit of cobalt in mercury chalcogenides, this group of narrow-gap II-VI DMS has been obtained in the 1990s and even today their properties are not well known and understood. Magnetic properties of  $\text{Hg}_{1-x}\text{Co}_x\text{Se}$  crystals have already been investigated.<sup>10,11</sup> However, because of the presence of Co-related ferromagnetic precipitates evidenced in Refs. 10,12, and 13 as well as of Co-related ionic clusters reported in Refs. 14 and 15 all numerical data concerning the  $\text{Co}^{2+}$ - $\text{Co}^{2+}$  exchange interaction in this DMS should be treated with caution. Under these circumstances, there exists a clear need of new experimental data for another narrow-gap II-VI DMS containing Co, particularly if it is a pure zincblende single-phase material.

The goal of the present work was to study the *d-d* interactions between magnetic impurities within the framework of the extended nearest-neighbor pair approximation (EN-NPA). Details of this model will be discussed later (Sec. II). For this study we used  $\text{Hg}_{1-x}\text{Co}_x\text{S}$  mixed crystals which fulfill all the requirements above mentioned.

The zincblende phase of mercury sulphide ( $\beta$ -HgS) is a metastable modification of this compound. Together with HgTe and HgSe it belongs to the family of zero-gap mercury chalcogenides. For these semimetals the  $\Gamma_6$  and  $\Gamma_8$  levels show an inverted ordering which results in the inverted band structure at the center of the Brillouin zone with a negative value of the energy gap defined as  $E_0 = E(\Gamma_6) - E(\Gamma_8)$ . Details of the band structure of  $\beta$ -HgS are discussed elsewhere.<sup>16</sup>

The addition of selected transition-metal atoms into the mercury sulfide corresponding to more than about 0.02 of the molar fraction stabilizes the zincblende phase in the resulting mixed crystals, as it is the case for Mn, Fe, and Co.<sup>17-20</sup> According to the present knowledge, the  $\text{Hg}_{1-x}\text{Co}_x\text{S}$  can be grown up to the mixed crystal composition equal to at least

$x=0.07$ .<sup>20</sup> Moreover, possible clustering of Co-related defects or creation of magnetic precipitates in this DMS has not been reported in the literature. Results of x-ray diffraction studies performed in Ref. 20 did not reveal a presence of other phases like, e.g., Co-related precipitates or CoS clusters. It should be stressed that CoSe clusters have been observed by the same technique in  $\text{Hg}_{1-x}\text{Co}_x\text{Se}$  crystals with the Co content as low as  $x=0.01$ .<sup>13</sup>

## II. MODEL

Each  $\text{Co}^{2+}$  ion is surrounded by four  $\text{S}^{2-}$  ions, in the axions forming a regular tetrahedron. The free  $\text{Co}^{2+}$  ion possess a  $3d^7$  configuration leading to a  $^4F$  ground state with nonvanishing orbital momentum ( $S=3/2$ ,  $L=3$ ). The splitting of this atomic term induced by the crystal field and the spin-orbit interaction results in a high energy separation between the ground and the first excited state equal to approximately 5000 K. Thus, at any experimentally accessible temperature the excited states cannot be populated. Due to this fact, the magnetic properties of Co-based DMS are governed by the ground state which is the orbital singlet and the spin quartet  $^4A_{2g}$ . As it has been shown previously (see, e.g., Refs. 4 and 5) the spin moment only equal to  $S=3/2$  allows an adequate description of the system. Within this approach the only influence due to the neglected excited states manifests in the deviation of the  $g$  factor from its free-ion value ( $g=2.234$ ).

Within the mean-field approximation and for the high-temperature regime the static magnetic susceptibility can be expressed in the form of the Curie-Weiss law:<sup>21</sup>

$$\chi = C(x)/(T - \Theta_0 x), \quad (1)$$

where  $C(x) = N_{Av} x (g \mu_B)^2 S(S+1) / [3k_B m(x)]$  is the Curie constant ( $N_{Av}$  is Avogadro's number,  $g$  is the Co Landé factor,  $\mu_B$  is the Bohr magneton,  $S$  is the total spin,  $k_B$  is the Boltzmann constant, and  $m(x)$  is the molar mass) and  $\Theta_0$  is the Curie-Weiss temperature for the hypothetical CoS in the zincblende phase. The Curie-Weiss temperature is given by the infinite series of exchange integrals  $J_\nu$  for pairs of  $\nu$ th neighbors weighted by  $z_\nu$ , the number of cations on the  $\nu$ th coordination sphere around a chosen central ion:

$$\Theta_0 = -\frac{2}{3} S(S+1) \sum_{\nu} J_\nu z_\nu / k_B. \quad (2)$$

Co-based DMS can be treated as a random system of localized magnetic moments, coupled by the long-range exchange interactions. Thus, the magnetic properties of the system can be calculated using the ENNPA model. In this model the partition function is factorized into separate contributions of interacting pairs of moments.<sup>4,8,22,23</sup> Each pair is formed between a central fixed ion and another ion distributed on a given coordination sphere. Both ions interact according to the power law  $J_\nu = J_{NN} / R_\nu^n$ . Moreover, not only pairs but also open triangles can be easily incorporated into this model. The appropriate Hamiltonians for the above-mentioned systems can be found in Ref. 24. The calculated

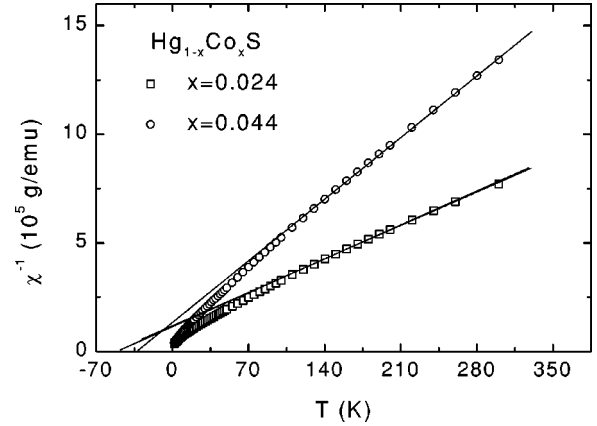


FIG. 1. High-temperature dependence of the inverse susceptibility. symbols, experimental data; solid lines, linear fit in high-temperature region.

partition function permits to determine directly all the thermodynamic properties of the material.

## III. EXPERIMENT

The crystals investigated in the present work were grown at the Institute of Physics of the Polish Academy of Sciences in Warsaw by the modified Bridgman method. Details of the crystal growth are presented elsewhere.<sup>19,20</sup> Two ingots of nominal composition  $x=0.02$  and  $0.04$  were prepared using pure binary compounds HgS and CoS in respective molar fractions. The crystals quality were checked by x-ray diffraction, scanning electron microscopy SEM microprobe, and by the energy-dispersive x-ray fluorescence (EDXRF). The mixed crystal composition determined using Vegard's law for various parts of the ingots does not differ from the nominal one by more than 20% (these differences are due to the chemical segregation). However, other phases (cinnabar phase of the pure mercury sulfide or the mixed crystals and/or cobalt-related precipitates like, e.g., CoS, etc.) have not been found in all investigated crystals within the detection limit of the applied characterization techniques.

Measurements of the dc magnetic susceptibility were carried out using a superconducting quantum interference device (SQUID) magnetometer in the temperature range 1.8 K–300 K in the presence of low external magnetic field. The magnetization data were collected in magnetic fields up to 50 kOe at two temperatures: 1.8 K and 3.0 K. The diamagnetic contribution<sup>18</sup> for HgS in the zincblende phase ( $\chi_d = -3.2 \times 10^{-7}$  emu/g) was subtracted from the susceptibility and magnetization data.

## IV. RESULTS AND DISCUSSION

The results of the inverse magnetic susceptibility of two  $\text{Hg}_{1-x}\text{Co}_x\text{S}$  samples versus temperature are shown in Fig. 1. The nominal mixed crystal compositions were equal to  $x=0.02$  and  $x=0.04$ . Open squares and open circles correspond to the experimental data, while solid lines represent the linear fit to these data in the high-temperature range from 120 K to 300 K. This fit unambiguously evidences an anti-

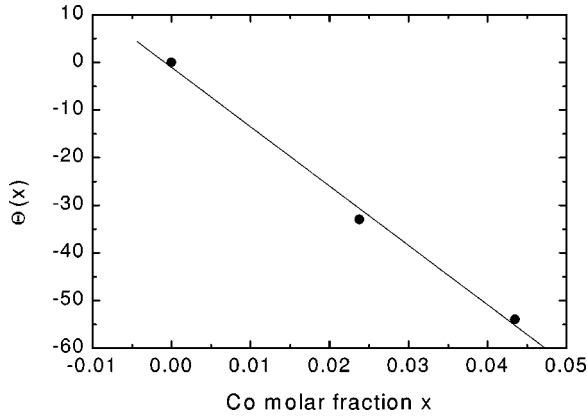


FIG. 2. Curie-Weiss temperature versus cobalt molar fraction.

ferromagnetic character of the exchange interaction between Co ions (negative Curie-Weiss temperature). This is also a direct proof that our samples do not contain ferromagnetic inclusions (a presence of ferromagnetic precipitates leads to the positive Curie temperature in the case of  $\text{Hg}_{1-x}\text{Co}_x\text{Se}$  crystals, as it has been demonstrated in Ref. 10).

From the linear fit to  $\text{Hg}_{1-x}\text{Co}_x\text{S}$  data in the high-temperature range in Fig. 1 the value of the Curie constant and Curie-Weiss temperature were determined. The sample compositions obtained from Curie constant were equal to  $x=0.024$  and  $x=0.044$ , respectively. These values are used as a real mixed crystal compositions along the paper.

The dependence of the antiferromagnetic Curie-Weiss temperature on the crystal composition is shown in Fig. 2. From this linear dependence a value of  $\Theta_0 = -1246$  K for pure CoS in the hypothetical zincblende phase was obtained. Using  $J_{eff}$  in Eq. (2), instead of series expansion, one can obtain an upper estimate of the effective nearest-neighbor interaction strength as  $J_{eff} = -42 \text{ K} \pm 5 \text{ K}$ . On the other hand, when summation in Eq. (2) is performed up to 20 coordination spheres, one gets  $J_{NN} = -31 \text{ K} \pm 4 \text{ K}$ .

The temperature dependence of measured magnetic susceptibility is shown in Fig. 3 by symbols. The magnetic field dependence of the experimental magnetization at two tem-

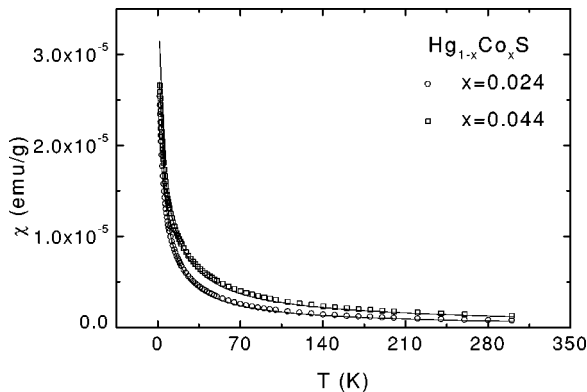


FIG. 3. Temperature dependence of the susceptibility for two samples of  $\text{Hg}_{1-x}\text{Co}_x\text{S}$ . Solid lines indicate theoretical results within the ENNPA model ( $J_{NN} = -33$  K and  $n=5$ ); symbols indicate experimental data.

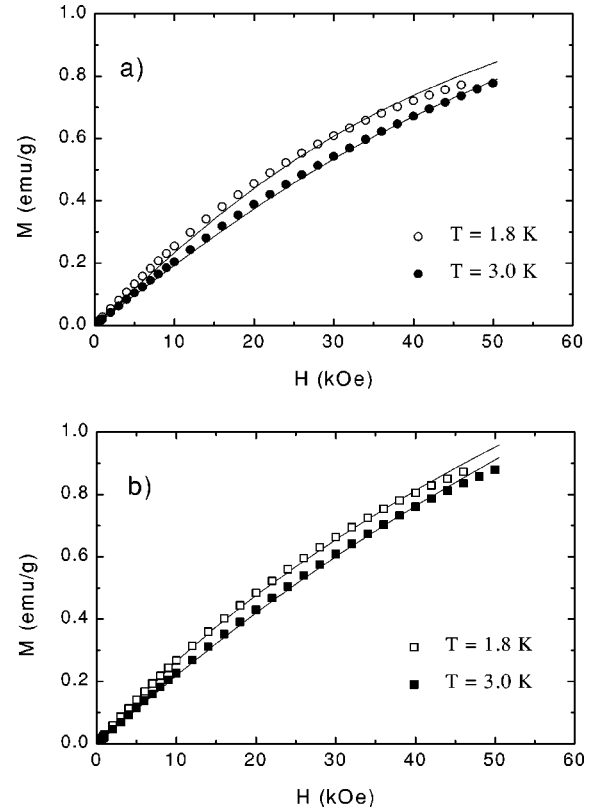


FIG. 4. Magnetization of  $\text{Hg}_{1-x}\text{Co}_x\text{S}$  a)  $x=0.024$ , b)  $x=0.044$ . Solid lines indicate theoretical results within the ENNPA model ( $J_{NN} = -33$  K and  $n=5$ ), symbols – experimental data.

peratures is presented also by symbols in Figs. 4(a) and 4(b). The solid lines in both figures correspond to the results of simultaneous least squares fit of theoretical curves to the data performed within the ENNPA model.

When the fit was performed with  $J_{NN}$  and  $n$  as variables the following limits for these value were obtained:  $-35 \text{ K} < J_{NN} < -32 \text{ K}$ ,  $4.96 < n < 5.03$ . The last finding provides a remarkably high accuracy to the value of the power-law exponent  $n=5$  theoretically predicted previously.<sup>6,7</sup> It should be also pointed out that the value of  $n$  determined for zincblende  $\text{Hg}_{1-x}\text{Co}_x\text{S}$  from ENNPA model is exactly the same as that corresponding to Mn impurity in all the three mercury chalcogenides.<sup>9,23</sup> It means that the exchange interactions between Co and between Mn ions in these materials are governed by the same mechanism, proposed in Refs. 6 and 7. One can state then that the radial dependence of the exchange interaction strength behaves according to the power law with the exponent  $n=5$  and this is a general property for narrow-gap DMS. It is worth mentioning that in the case of the Mn-based wide-gap DMS this exponent inferred from experimental data<sup>8</sup> as well as theoretically predicted<sup>7</sup> equals at least 6.8 or is even higher.

The comparison between the exchange integrals for Mn-based and Co-based wide-gap II-VI DMS<sup>3-5,25-28</sup> showed that the  $J_{NN}$  exchange integral is from three to four times greater in the case of mixed crystals containing Co. The same ratio was obtained from the comparison of the present result for  $J_{NN}$  with the appropriate value for  $\text{Hg}_{1-x}\text{Mn}_x\text{S}$ .<sup>9</sup>

This is an additional evidence of much stronger antiferromagnetic coupling between Co ions than that between Mn ions.

## V. CONCLUSIONS

We have presented here a consistent interpretation of the magnetic susceptibility and the magnetization data for  $\text{Hg}_{1-x}\text{Co}_x\text{S}$  in the extended nearest-neighbor pair approximation. The exchange coupling constant for Co ions in  $\text{Hg}_{1-x}\text{Co}_x\text{S}$  ( $J_{\text{NN}} = -33$  K) is roughly four times larger than that for Mn ions in  $\text{Hg}_{1-x}\text{Mn}_x\text{S}$  ( $J_{\text{NN}} = -7.7$  K), which is in accordance with the trend observed between Co-based wide-gap DMS and their Mn-based counterparts. On the other hand, we have shown that the long-range character of exchange interaction and its decay with distance are identical

for both Mn and Co ions, which may indicate that it is intrinsic characteristics of narrow gap DMS's.

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- <sup>1</sup>*Diluted Magnetic Semiconductors*, in *Semiconductors and Semimetals series*, Vol. 25, edited by J.K. Furdyna and J. Kossut (Academic Press, Boston, 1988).
- <sup>2</sup>J. Kossut and W. Dobrowolski, in *Handbook of Magnetic Materials*, edited by K.H.J. Buschow (Elsevier, Amsterdam, 1993), Vol. 7, p. 231.
- <sup>3</sup>T.M. Giebultowicz, J.J. Rhyne, J.K. Furdyna, and P. Klosowski, *J. Appl. Phys.* **65**, 5096 (1990).
- <sup>4</sup>A. Lewicki, A. I. Schindler, J. K. Furdyna, and T. M. Giebultowicz, in *Diluted Magnetic Semiconductors*, edited by M. Jain (World Scientific, Singapore, 1991), p. 409.
- <sup>5</sup>A. Twardowski, H. J. M. Swagten, and W. J. M. de Jonge, in *II-VI Semiconductor Compounds*, edited by M. Jain (World Scientific, Singapore, 1993), p. 227.
- <sup>6</sup>V.K. Dugaev and V.I. Litvinov, *Phys. Rev. B* **41**, 788 (1990).
- <sup>7</sup>T. Rusin (unpublished).
- <sup>8</sup>A. Twardowski, H.J.M. Swagten, W.J.M. de Jonge, and M. Demianiuk, *Phys. Rev. B* **36**, 7013 (1987).
- <sup>9</sup>K. Dybko, W. Szuszkiewicz, F. Palacio, E. Dynowska, W. Paszkowicz, and B. Witkowska, *J. Magn. Magn. Mater.* **192**, 61 (1999).
- <sup>10</sup>M. Averous, C. Fau, S. Charar, M.El. Kholdi, V.D. Ribes, J. Deportes, and Z. Gołacki, *Solid State Commun.* **84**, 479 (1992).
- <sup>11</sup>W. Szuszkiewicz, M. Arciszewska, B. Witkowska, C. Julien, and M. Balkanski, *J. Magn. Magn. Mater.* **140-144**, 2037 (1995).
- <sup>12</sup>M. Averous, C. Fau, S. Charar, M.El. Kholdi, V.D. Ribes, J. Deportes, and Z. Gołacki, *Phys. Rev. B* **47**, 10 261 (1993).
- <sup>13</sup>J. Kachniarz, E. Dynowska, S. Miotkowska, B. Witkowska, C. Julien, and W. Szuszkiewicz, in *Proceedings of the XVI Conference on Applied Crystallography*, Cieszyn 1994, edited by H. Morawiec and D. Stróż (World Scientific, Singapore, 1995), p. 317.
- <sup>14</sup>V.D. Prozorovskii, I.Yu. Reshidova, and Yu.S. Paranchich, *Fiz. Nizk. Temp.* **21**, 576 (1995) [*Low Temp. Phys.* **21**, 449 (1995)].
- <sup>15</sup>E.A. Neifeld, K.M. Demchuk, G.I. Kharus, A.E. Bubnova, L.I. Domanskaya, G.D. Shtrapein, and S.Yu. Paranchich, *Fiz. Tekh. Poluprovodn.* **31**, 318 (1997) [*Sov. Phys. Semicond.* **31**, 261 (1997)].
- <sup>16</sup>K. Dybko, W. Szuszkiewicz, E. Dynowska, W. Paszkowicz, and B. Witkowska, *Physica B* **256-258**, 629 (1998).
- <sup>17</sup>A. Pajęczkowska and A. Rabenau, *J. Solid State Chem.* **21**, 43 (1979).
- <sup>18</sup>V. Spasojevic, D. Rodic, P. Nordblad, and A. Bajorek, *J. Magn. Magn. Mater.* **118**, 152 (1993).
- <sup>19</sup>K. Dybko, W. Szuszkiewicz, and B. Witkowska, *Defect Diffus. Forum* **121-122**, 41 (1995).
- <sup>20</sup>W. Szuszkiewicz, E. Dynowska, P. Dłużewski, W. Paszkowicz, A. Szczepańska, and B. Witkowska, *Phys. Status Solidi B* **229**, 73 (2001).
- <sup>21</sup>J. Spałek, A. Lewicki, Z. Tarnawski, J.K. Furdyna, R.R. Gałazka, and Z. Obuszko, *Phys. Rev. B* **33**, 3407 (1986).
- <sup>22</sup>K. Matho, *J. Low Temp. Phys.* **35**, 165 (1979).
- <sup>23</sup>C.J.M. Denissen and W.J.M. de Jonge, *Solid State Commun.* **59**, 503 (1986).
- <sup>24</sup>S. Oseroff and P.H. Keesom, in *Semiconductors and Semimetals*, edited by J. K. Furdyna and J. Kossut (Academic Press, Boston, 1988), Vol. 25, p. 73.
- <sup>25</sup>T.Q. Vu, V. Bindilatti, Y. Shapira, E.J. McNiff, Jr., C.C. Agosta, J. Papp, R. Kershaw, K. Dwight, and A. Wold, *Phys. Rev. B* **46**, 11 617 (1992).
- <sup>26</sup>S. Foner, D. Heiman, T.Q. Vu, T. Fries, G.H. McCabe, Y. Shapira, and M. Demianiuk, *Solid State Commun.* **95**, 455 (1995).
- <sup>27</sup>M. Dahl, D. Heiman, S. Foner, T.Q. Vu, R. Kershaw, K. Dwight, and A. Wold, *Phys. Rev. B* **51**, 17 561 (1995).
- <sup>28</sup>H. Alawadhi, I. Miotkowski, A. Lewicki, A.K. Ramdas, S. Miotkowska, and M. McElfresh, *J. Phys.: Condens. Matter* **14**, 4611 (2002).