

Magnetic Behaviour of the Ce–Co–Mn Intermetallics of MgCu₂ Structure Type

R. DUDRIC^a, A. POPESCU^a, O. ISNARD^b, V. POP^a AND M. COLDEA^{a,*}

^aBabes-Bolyai University, Faculty of Physics, Kogalniceanu Str. 1, 400084, Cluj-Napoca, Romania

^bInstitut Néel du CNRS, Université Joseph Fourier, 38042 Grenoble, Cedex 9, France

(Received November 6, 2014; in final form March 25, 2015)

The magnetic properties of CeCoMn, Ce₃Co₃Mn₄ and Ce₃Co₆Mn alloys have been investigated by magnetization and susceptibility measurements in the temperature range (5–300) K and magnetic field up to 12 T. X-ray powder diffraction measurements showed that all three alloys are isostructural and crystallize in the cubic MgCu₂ structure type. Both Ce and Co atoms are non-magnetic in all alloys like in the isostructural compound CeCo₂. Magnetic behavior of the investigated alloys is mostly due to the Mn moments and depends essentially on the Mn–Mn distances. The interaction between the Mn moments is antiferromagnetic in CeCoMn and Ce₃Co₃Mn₄ but a paramagnetic behavior for Ce₃Co₆Mn was evidenced in the studied temperature range.

DOI: [10.12693/APhysPolA.128.67](https://doi.org/10.12693/APhysPolA.128.67)

PACS: 71.20.Eh, 75.20.En, 75.20.Hr, 75.30.Cr

1. Introduction

In the ternary metallic system Ce–Co–Mn, many intermetallic compounds and alloys with different crystallographic structures are reported [1]. The nearest-neighborhood of Co and Mn atoms, as well as, the Co–Co, Co–Mn, and Mn–Mn distances are different in each compound. By combining X-ray photoelectron spectroscopy (XPS) and magnetic measurements, we have shown that in Ce₂Co₁₅Mn₃ (with Th₂Zn₁₇ structure type) [2] and CeCo₇Mn₅ and CeCo₈Mn₄ (with ThMn₁₂ structure type) [3] compounds both Co and Mn atoms carry magnetic moments and Ce atoms are in the intermediate valence state. The complex magnetic structure of the three compounds is determined by the competition between the ferromagnetic (Co–Co pairs) and antiferromagnetic (Co–Mn and Mn–Mn pairs) interactions.

According to Pearson's handbook of crystallographic data for intermetallic phases, three intermetallic compositions CeCoMn, Ce₃Co₃Mn₄ and Ce₃Co₆Mn have been reported to crystallize in the MgCu₂ structure type and are isostructural with the parent compound CeCo₂ [1]. Earlier studies on the magnetic properties of CeCo₂ have shown that this compound is an enhanced Pauli paramagnet [4–6]. The magnetic susceptibility of CeCo₂ corrected for ferromagnetic impurities [6, 7] and additionally for the Curie–Weiss term attributed to Ce³⁺ impurity ions (about 3%) is almost constant in the temperature range (4–300) K [8]. The low magnetic susceptibility and relatively weak temperature dependence, with values in the range $(1–1.3) \times 10^{-3}$ emu/mol, indicates that in this compound both Ce and Co atoms are non-magnetic. It was also shown that this slightly

temperature dependence of the intrinsic magnetic susceptibility is due to the fine structure of the density of states in the vicinity of E_F [7]. XPS and X-ray absorption edge studies have shown that only the Ce⁴⁺ valence state is present in the bulk of CeCo₂, while both Ce³⁺ and Ce⁴⁺ valence states coexist on the surface of CeCo₂ [9]. The theoretical calculations have brought out strong hybridization of the itinerant $4f$ (Ce) and $3d$ (Co) states, which leads to a filling of the peculiar bonding band. It is demonstrated that the magnetic properties of CeCo₂ are consistent with itinerant behavior of the $4f$ electrons of Ce [10–13]. In CeCo₂, both the strongly correlated $4f$ -electrons and $3d$ -electrons contribute to the enhanced Pauli susceptibility [14]. The reported experimental data and the theoretical studies infer that CeCo₂ compound is an exchange-enhanced Pauli paramagnet with a spin fluctuation temperature T_{sf} higher than room temperature and this is consistent with the almost temperature independent magnetic susceptibility below room temperature [6–8].

The aim of this paper is to study the influence of Mn on the magnetic properties of the parent compound CeCo₂ by correlating the results obtained from XRD and magnetic measurements as a function of field and temperature. The Anderson condition for the existence of the local moment at a transition metal site (T) when solute in another transition metal is $\pi\Delta/U < 1$, where Δ is the width of the d states (corresponds to the virtual bound states in the Friedel model [15] and U is the Coulomb correlation energy between d electrons [16]. It was found experimentally that this condition is fulfilled in many intermetallic compounds and alloys based on Mn [17–32]. It is worth mentioning here that the Mn-based alloys and compounds are assumed to exhibit a strong dependence of Mn–Mn exchange interaction as a function of distance between the nearest-neighbor Mn atoms. It is well known that the Mn–Mn interaction is antiferromagnetic when the distance d_{Mn-Mn} is smaller than the critical value

*corresponding author; e-mail:

roxana.pacurariu@phys.ubbcluj.ro

of $d_{\text{cr}} \approx 2.8 \text{ \AA}$. Typical examples are the antiferromagnetic compounds XMn ($X = \text{Ni, Pd, Pt}$) [17–20], RMn_2 ($R = \text{Y, Pr, Nd, Sm, Gd, Tb}$) [21, 22], RMn_{12} ($R = \text{Y}$ and heavy rare earths) [23] with $d_{\text{Mn-Mn}} < d_{\text{cr}}$.

2. Experimental

The alloys CeCoMn , $\text{Ce}_3\text{Co}_3\text{Mn}_4$ and $\text{Ce}_3\text{Co}_6\text{Mn}$ were prepared by argon arc melting. The samples were melted repeatedly in the same atmosphere to ensure homogeneity. The purity of the starting materials was 99.9% for all the constituent elements. The crystalline structure of the samples was analyzed at room temperature by using a D 5000 Brücker Bragg-Brentano diffractometer with $\text{Cu K}\alpha$ radiation. The magnetic measurements were performed in the temperature range 5–300 K and magnetic field up to 12 T using a vibrating sample magnetometer VSM from Cryogenics.

XRD measurements showed that CeCoMn , $\text{Ce}_3\text{Co}_3\text{Mn}_4$ (or $\text{CeCoMn}_{1.33}$) and $\text{Ce}_3\text{Co}_6\text{Mn}$ (or $\text{CeCo}_2\text{Mn}_{0.33}$) are single phases and crystallize in the cubic MgCu_2 structure type (Fig. 1). This is in agreement with the recently reported results on RCo_2Mn ($R = \text{Ho}$ and Er) [31] and RNi_2Mn with $R = \text{Tb, Dy, Ho, Er}$ alloys [32], which crystallize in the MgCu_2 -type structure and are isostructural to RCo_2 and, respectively, RNi_2 compounds. Both these studies have shown the presence of vacancies in the crystallographic structure and that the excess Mn occupies both the R and the Co/Ni atomic positions.

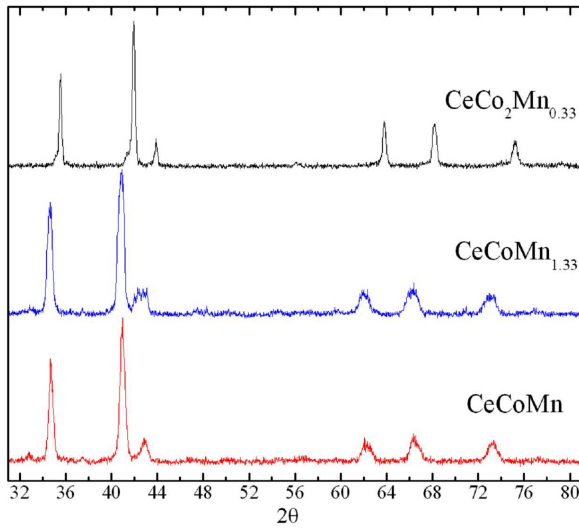


Fig. 1. X-ray diffraction pattern of CeCoMn , $\text{CeCoMn}_{1.33}$ and $\text{CeCo}_2\text{Mn}_{0.33}$ recorded using the $\text{Cu K}\alpha$ radiation.

At room temperature, the lattice parameters for the investigated compounds are: $a = 7.30 \text{ \AA}$ for CeCoMn , $a = 7.33 \text{ \AA}$ for $\text{CeCoMn}_{1.33}$ and $a = 7.16 \text{ \AA}$ for $\text{CeCo}_2\text{Mn}_{0.33}$, in good agreement with the values reported in the literature [1]. The lattice parameter of the parent compound CeCo_2 was found to be $a = 7.16 \text{ \AA}$ [1]. Since the atomic radius of Mn atoms is larger than that of

Co atoms (1.307 \AA and 1.252 \AA , respectively), the lattice parameter of compounds with higher Mn content are larger than that of CeCo_2 . In the parent compound CeCo_2 , the Ce and Co atoms occupy the $8a$ sites (0,0,0) and $16d$ ($5/8, 5/8, 5/8$), respectively. In the investigated compounds the Mn atoms occupy both Ce and Co sites. The minimum distance between Mn atoms is $d_{\text{Mn-Mn}} < 2.6 \text{ \AA}$ for both Mn atoms occupying $16d$ sites, while for Mn atoms in the $8a$ sites the $d_{\text{Mn-Mn}} > 2.9 \text{ \AA}$. Due to the smaller number of Mn atoms in the unit cell, the average distance $d_{\text{Mn-Mn}}$ in $\text{CeCo}_2\text{Mn}_{0.33}$ is much larger than that in the isostructural CeCoMn and $\text{CeCoMn}_{1.33}$ alloys.

3. Results and discussions

Figure 2 shows the temperature dependence of the zero field cooled (ZFC) magnetization for $\text{CeCoMn}_{1.33}$ measured in two applied magnetic fields $B = 1 \text{ T}$ and 2 T . The $M(T)$ curves exhibit a maximum around 44 K and 35 K, respectively, revealing the antiferromagnetic behavior of $\text{CeCoMn}_{1.33}$ alloy. This maximum shifts to lower temperatures when the magnetic field increases, suggesting a first order character of the magnetic transition antiferromagnetic–paramagnetic at T_N . In order to confirm this assumption, further investigations like volume, resistivity and/or specific heat versus temperature measurements are necessary. Similar $M(T)$ dependences, with transition temperatures closed on those observed in $\text{CeCoMn}_{1.33}$, were obtained for CeCoMn compound. Since the Ce and Co atoms do not carry any ordered magnetic moment, like in CeCo_2 , the magnetic behaviour of these alloys is due to the interactions between the Mn local moments. The nearest-neighbour Mn–Mn distance between Mn atoms in both alloys is about 2.6 \AA , smaller than the critical value, which explains the antiferromagnetic interaction between the neighbouring Mn atoms. The isostructural compound YMn_2 , with $d_{\text{Mn-Mn}} = 2.73 \text{ \AA}$, has been shown to be an antiferromagnet with $\mu = 2.7 \mu_B/\text{Mn}$ and $T_N = 100 \text{ K}$ [33, 34].

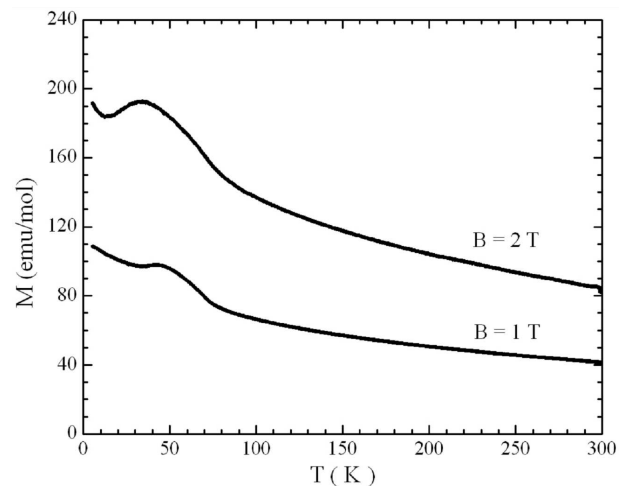


Fig. 2. Temperature dependence of the magnetization for $\text{CeCoMn}_{1.33}$ measured in the ZFC state with applied fields of 1 T and 2 T.

The upturn of the $M(T)$ curves at lower temperatures is due to traces of magnetic impurities, possible to some Co clusters. The $M(B)$ curves at 5 K show a small concavity towards field axis at low fields, followed by a linear high field regime, revealing both the presence of a ferromagnetic component, which saturates at lower fields, and the antiferromagnetic behavior of CeCoMn and CeCoMn_{1.33} alloys. The extrapolation of the linear $M(B)$ dependence to $B = 0$ gives for the spontaneous magnetizations of the ferromagnetic components the values around $0.01 \mu_B/\text{f.u.}$ in both alloys. Supposing a value of $1.7 \mu_B/\text{Co}$, like in metallic Co, the magnetic impurities represent less than 1% from the total number of Co atoms. toward the temperature axis (Fig. 5 — open circles)

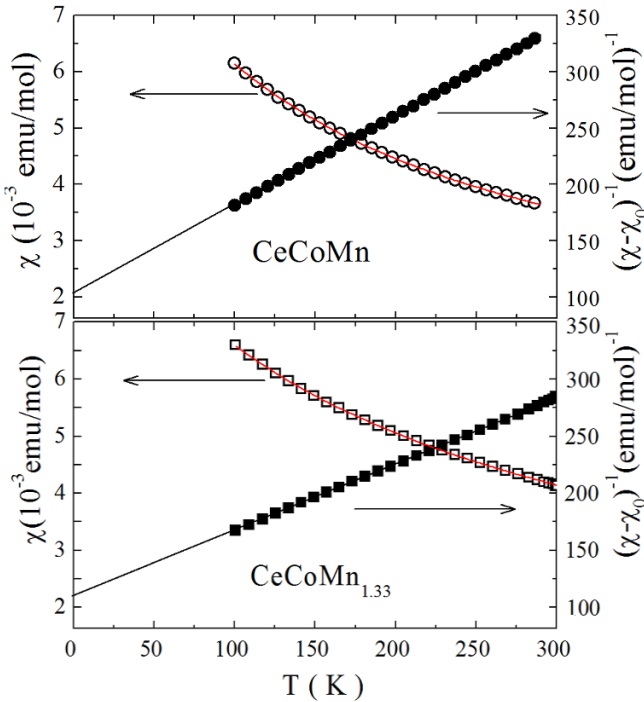


Fig. 3. Magnetic susceptibility and reciprocal magnetic susceptibility versus temperature for CeCoMn and CeCoMn_{1.33} alloys; the curve fitting results (solid lines) are superposed on the measured data.

The magnetic susceptibilities of CeCoMn and CeCoMn_{1.33} for $T > 100$ K (Fig. 3) may be described by the Curie–Weiss law: $\chi = C/(T - \theta) + \chi_0$, as one can see from the linear temperature dependences of $(\chi - \chi_0)^{-1}$. The pure Curie–Weiss term $C/(T - \theta)$ is attributed to Mn magnetic moments whereas χ_0 originate essentially from the itinerant $4f$ (Ce) and $3d$ (Co) states. The parameters obtained from curve fitting are: $C = 1.203$ K emu/mol; $\theta = -122.1$ K and $\chi_0 = 0.72 \times 10^{-3}$ emu/mol for CeCoMn and $C = 1.720$ K emu/mol; $\theta = -188.3$ K and $\chi_0 = 0.63 \times 10^{-3}$ emu/mol for CeCoMn_{1.33}. The values of the effective magnetic moments, calculated from the Curie constants, are $\mu_{\text{eff}} = 3.12 \mu_B/\text{Mn}$ in CeCoMn and $\mu_{\text{eff}} = 3.22 \mu_B/\text{Mn}$ in CeCoMn_{1.33}. This is a clear

evidence of the local moments on Mn sites, in good agreement with the Anderson condition for the existence of local magnetic moments on T sites. Since the $d_{\text{Ce–Ce}}$, $d_{\text{Ce–Co}}$, and $d_{\text{Co–Co}}$ distances in all investigated alloys are very close to the corresponding distances in the parent compound CeCo₂, it is expected that the hybridization degree between the itinerant $4f$ (Ce) and $3d$ (Co) states remains practically constant and in consequence the electronic band structure near E_F of the investigated alloys is almost unchanged relative to that of CeCo₂. The Co and Ce atoms are non-magnetic in the investigated alloys, like in CeCo₂, and due to a high value of the spin fluctuation temperature T_{sf} , they have no contribution to the temperature dependence of the susceptibility below room temperature. One can observe that values obtained for the effective magnetic moments of Mn atoms in the two alloys are close. In the ordered magnetic state, these values corresponds to a magnetic moment $\mu \approx 2.35 \mu_B/\text{Mn}$, which is slightly smaller than for the isostructural compound YMn₂. This is to be expected considering that the $d_{\text{Mn–Mn}}$ distances in the investigated alloys are smaller than those in YMn₂. One can also remark that the increase of the paramagnetic Curie temperature θ bears witness to the increase of the overall dominant antiferromagnetic interactions.

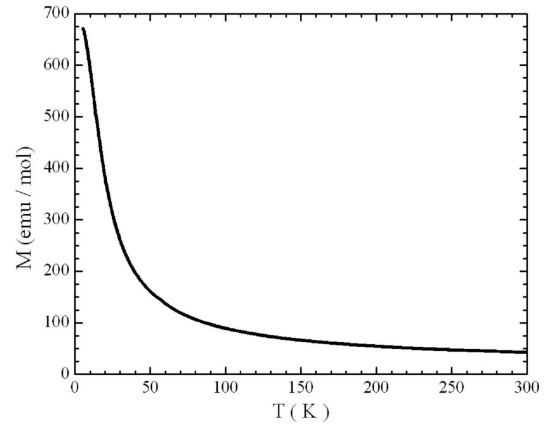


Fig. 4. Temperature dependence of magnetization for CeCo₂Mn_{0.33} in 1 T magnetic field.

The magnetization as a function of temperature for CeCo₂Mn_{0.33} (Fig. 4), measured in a magnetic field $B = 1$ T, reveals the paramagnetic behavior of this alloy in the investigated temperature range.

The reciprocal magnetic susceptibility of CeCo₂Mn_{0.33} alloy shows a pronounced concavity, suggesting the presence in the measured susceptibility of an important temperature independent contribution χ_0 . Indeed, the magnetic susceptibility may be described within the modified Curie–Weiss law, $\chi = C/(T - \theta) + \chi_0$, for wide temperature range, as one can see from the linear dependence of $(\chi - \chi_0)^{-1}$ versus temperature (shown also in Fig. 5 — stars). The fit parameters are as follows: $C = 0.706$ K emu/mol; $\chi_0 = 1.9 \times 10^{-3}$ emu/mol and $\theta \approx -1$ K. The Curie–Weiss term is due to the Mn local magnetic moments like for the isostructural com-

pounds CeCoMn and CeCoMn_{1.33}. From the Curie constant results the value of the effective magnetic moment $\mu_{\text{eff}} = 4.1 \mu_{\text{B}}/\text{Mn}$. The value of the paramagnetic Curie temperature suggests that the interaction between the Mn local magnetic moments in CeCo₂Mn_{0.33} is negligible. This was to be expected due to a larger distance between the Mn moments in comparison with that found in the other two alloys CeCoMn and CeCoMn_{1.33}, which are much richer in Mn. In the case of CeCo₂Mn_{0.33} alloy, the Mn atoms are diluted in the CeCo₂ matrix and consequently are only expected to be found as second near neighbours. It is to note that the value of the Mn effective magnetic moment in CeCo₂Mn_{0.33} alloy is very close to that calculated in the cluster model for Mn impurities in non-magnetic metals, namely $4.04 \mu_{\text{B}}/\text{Mn}$ [35, 36].

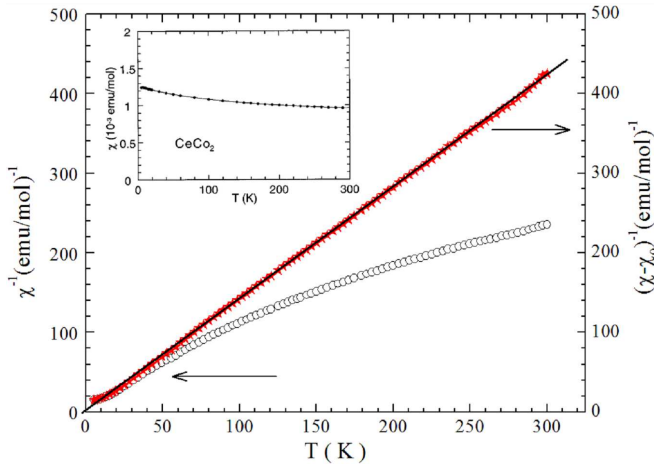


Fig. 5. Reciprocal magnetic susceptibility versus temperature for CeCo₂Mn_{0.33}. In the inset there is shown the temperature dependence of the intrinsic magnetic susceptibility of CeCo₂ [6].

It is worth mentioning here that the value of χ_0 for all three alloys are of the order of susceptibility for the parent compound CeCo₂ [6–8]. The temperature independent susceptibility χ_0 may be expressed as: $\chi_0 = S\chi_{\text{P}} + \chi_{\text{orb}} + \chi_{\text{dia}} + \chi_{\text{L}}$, where $\chi_{\text{P}} = \mu_{\text{B}}^2 N(E_{\text{F}})$ is the Pauli spin susceptibility, $S = 1/[1 - IN(E_{\text{F}})]^{-1}$ is the Stoner enhancement factor, I is the effective exchange-correlation interaction between the conduction electrons, χ_{orb} represents the orbital Van-Vleck-like susceptibility, χ_{dia} — the diamagnetic susceptibility of core electrons and χ_{L} — the Landau diamagnetic susceptibility of the conduction electrons. The last three contributions in χ_0 are expected to be small in comparison with the strongly enhanced spin susceptibility. In CeCo₂, the Stoner enhancement factor was estimated to be $S \approx 5$ [7]. The smaller values of χ_0 in CeCoMn and CeCoMn_{1.33} in comparison with the corresponding values found in CeCo₂ and CeCo₂Mn_{0.33} may be explained by a weakness of the exchange-correlation interaction between the Co d electrons due to the changes in the first neighborhood of the Co atoms.

4. Conclusions

The partial substitution of Co by Mn in CeCo₂ and the supplementary addition of Mn to the parent compound conserve the MgCu₂ structure type and have significant effects on the magnetic behavior of the three investigated alloys. Magnetic behavior of the investigated alloys is mostly due to the local magnetic moments confined on Mn sites. The Ce and Co atoms are non-magnetic in all alloys like in the isostructural compound CeCo₂. The interaction between the Mn moments depends on the Mn–Mn distance and is antiferromagnetic in CeCoMn and CeCoMn_{1.33}, but is negligible in CeCo₂Mn_{0.33} determining a paramagnetic behaviour of this alloy in the (5–300) K temperature range. The temperature independent contribution in the magnetic susceptibility of CeCo₂Mn_{0.33} alloy is of the order of susceptibility for CeCo₂ compound.

Acknowledgments

This work was supported by the Romanian Ministry of Education and Research — UEFISCDI Project No. PN-II-ID-PCE-2012-4-0470 and Project No. PN-II-ID-PCE-2011-3-0583 (85/2011).

References

- [1] P. Vilars, L.D. Calvert, in: *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd ed., ASM International, Materials Park, OH 1991.
- [2] A. Popescu, O. Isnard, R. Dudric, M. Coldea, *J. Alloys Comp.* **535**, 10 (2012).
- [3] R. Dudric, A. Popescu, O. Isnard, M. Coldea, *Intermetallics* **38**, 150 (2013).
- [4] J.W. Ross, J. Crangle, *Phys. Rev.* **133A**, 509 (1964).
- [5] T.F. Smith, H.L. Luo, M.B. Maple, I.R. Harris, *J. Phys. F* **1**, 8961 (1971).
- [6] Y. Aoki, T. Nishigaki, H. Sugawara, H. Sato, *Phys. Rev. B* **55**, 27681 (1997).
- [7] A.S. Panfilov, G.E. Grechnev, I.V. Svechkarov, H. Sugawara, H. Sato, O. Eriksson, *Physica B* **319**, 268 (2002).
- [8] T.M. Seixas, J.M. Machado da Silva, *Physica B* **269**, 362 (1999).
- [9] C.N.R. Rao, D.D. Sarma, P.R. Sarode, R. Vijayaraghavan, S.K. Dhar, S.K. Malik, *J. Phys. C* **14**, L541 (1981).
- [10] O. Eriksson, L. Nordström, M.S.S. Brooks, B. Johansson, *Phys. Rev. Lett.* **60**, 2523 (1988).
- [11] H. Sugawara, M. Higuchi, O. Inoue, T. Nishigaki, Y. Aoki, H. Sato, R. Settai, Y. Onuki, A. Hasegawa, *J. Phys. Soc. Jpn.* **65**, 1744 (1996).
- [12] S. Tanaka, H. Harima, A. Yanase, *J. Phys. Soc. Jpn.* **67**, 1342 (1998).
- [13] G.E. Grechnev, *J. Low Temp. Phys.* **35**, 638 (2009).
- [14] S. Tanaka, H. Harima, *J. Phys. Soc. Jpn.* **67**, 2594 (1998).

- [15] J. Friedel, *Nuovo Cimento Suppl.* **2**, 287 (1958).
- [16] P.W. Anderson, *Phys. Rev.* **124**, 41 (1961).
- [17] L. Pal, E. Kren, G. Kadar, P. Szabo, T. Tarnoczi, *J. Appl. Phys.* **39**, 538 (1968).
- [18] A. Kjekshus, R. Mollerud, A.F. Andresen, W.B. Pearson, *Philos. Mag.* **16**, 1063 (1967).
- [19] A.F. Andresen, A. Kjekshus, R. Mollerud, W.B. Pearson, *Acta Chem. Scand.* **20**, 2529 (1966).
- [20] M. Coldea, M. Neumann, S.G. Chiuzbaian, V. Pop, L.G. Pascut, O. Isnard, A.F. Takacs, R. Pacurariu, *J. Alloys Comp.* **417**, 7 (2006).
- [21] H. Wada, H. Nakamura, K. Yoshimura, M. Shiga, Y. Nakamura, *J. Magn. Magn. Mater.* **70**, 134 (1987).
- [22] M. Shiga, *Physica B* **149**, 293 (1988).
- [23] J. Deportes, D. Givord, R. Lemaire, H. Nagai, *Physica* **86–88B**, 69 (1977).
- [24] R. Coehoorn, C. Haas, *Phys. Rev. B* **31**, 1980 (1985).
- [25] H. Kono, *J. Phys. Soc. Jpn.* **13**, 1444 (1958).
- [26] J.W. Cable, E.O. Wollan, W.C. Koehler, H.R. Child, *Phys. Rev.* **128**, 2118 (1962).
- [27] P.J. Webster, *Contemp. Phys.* **10**, 559 (1969).
- [28] R. Pacurariu, M. Coldea, M. Neumann, V. Pop, O. Isnard, M. Rakers, *Phys. Status Solidi B* **244**, 3190 (2007).
- [29] M. Coldea, M. Neumann, St. Lütkehoff, S. Mühl, R. Coldea, *J. Alloys Comp.* **278**, 72 (1998).
- [30] M. Coldea, V. Pop, M. Neumann, O. Isnard, R. Pacurariu, A.F. Takacs, L.G. Pascut, *Phys. Status Solidi B* **243**, 50 (2006).
- [31] V. Rednic, M. Coldea, S.K. Mendiratta, M. Valente, V. Pop, M. Neumann, L. Rednic, *J. Magn. Magn. Mater.* **321**, 3415 (2009).
- [32] R. Pacurariu, V. Rednic, M. Coldea, D. Benea, V. Pop, O. Isnard, M. Neumann, *Phys. Status Solidi B* **246**, 50 (2009).
- [33] Bibekananda Maji, K.G. Suresh, A.K. Nigam, *J. Magn. Magn. Mater.* **322**, 2415 (2010).
- [34] J.L. Wang, C. Marquina, M.R. Ibarra, G.H. Wu, *Phys. Rev. B* **73**, 094436 (2006).
- [35] P. Blaha, J. Callaway, *Phys. Rev. B* **33**, 1706 (1986).
- [36] D. Bagayoko, P. Blaha, J. Callaway, *Phys. Rev. B* **34**, 3572 (1986).