AIP Journal of Applied Physics

Crystal structure and physical properties of Gd 3 Co 4 Sn 13 intermetallic antiferromagnet

M. A. Pires, L. Mendonça Ferreira, J. G. S. Duque, R. R. Urbano, O. Agüero, I. Torriani, C. Rettori, E. M. Bittar, and P. G. Pagliuso

Citation: Journal of Applied Physics **99**, 08J311 (2006); doi: 10.1063/1.2173937
View online: http://dx.doi.org/10.1063/1.2173937
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/99/8?ver=pdfcov
Published by the AIP Publishing

Crystal structure and physical properties of $Gd_3Co_4Sn_{13}$ intermetallic antiferromagnet

M. A. Pires, L. Mendonça Ferreira, J. G. S. Duque, R. R. Urbano, O. Agüero, I. Torriani, C. Rettori, E. M. Bittar, and P. G. Pagliuso[a)]
Instituto de Física "Gleb Wataghin," UNICAMP, 13083-970, Campinas, Brazil

(Presented on 1 November 2005; published online 28 April 2006)

We have synthesized single crystalline samples of $Gd_3Co_4Sn_{13}$ intermetallic compound using a Sn-flux method. This compound crystallizes with a cubic $Yb_3Co_4Sn_{13}$-type structure, space group Pm-3*n*, which has 40 atoms per unit cell. Measurements of the magnetic susceptibility, heat capacity, electrical resistivity, and electron spin resonance (ESR) revealed that $Gd_3Co_4Sn_{13}$ is a metallic Curie-Weiss paramagnet at high temperature and presents an antiferromagnetic ordering below $T_N=14.5$ K. In the paramagnetic state, a single Gd^{3+} ESR line with a nearly temperature independent $g\sim2.005(2)$ is observed, and its linewidth follows a Korringa-like behavior as a function of temperature. From the Korringa rate ($\Delta H/\Delta T\sim4$ Oe/K) and *g*-shift ($\Delta g\sim0.012$) obtained from the ESR experiments combined with the magnetic susceptibility and specific heat data for $Gd_3Co_4Sn_{13}$, we have extracted the exchange parameters between the Gd^{3+} local moments and the conduction-electrons (c-e) in this compound. This exchange parameter $J_{fs}\approx10$ meV was found to be c-e wave-vector independent and the electronic structure of $Gd_3Co_4Sn_{13}$ has a single band character. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2173937]

I. INTRODUCTION

Systematic studies along the series of rare-earth-based intermetallic compounds are usually interesting to explore the interplay between Ruderman-Kittel-Kasuya-Yoshida (RKKY) magnetic interaction, crystalline electrical field (CEF) effects, and Fermi surface effects commonly present in these materials. For instance, the series of intermetallics $R_3M_4Sn_{13}$ [the so-called Remeika phases (3-4-13)] were systematically studied in the past, because despite their simple cubic structure, a large variety of interesting physical properties such as heavy-fermion (HF) behavior, conventional superconductivity (SC), and complex magnetic structures could be found in these series.[1–3] For $M=$Rh, many superconductors with T_c ranging between ~2.0 and ~9.0 K were reported.[2] Further, for $R=$Ce, the HF behavior has been observed for $M=$Rh, Ir, and also for an In-based variant $Ce_3Pt_4In_{13}$, with an electronic specific heat of the order of $\gamma=100-400$ mJ/mol K^2.[3,4] However, only very recently[5,6] the 3-4-13 materials with $M=$Co have become topic of scientific investigation revealing $La_3Co_4Sn_{13}$ as a conventional SC with $T_c=2.3$ K and $Ce_3Co_4Sn_{13}$ as a HF compound with unconventional low temperature behavior and a very large $\gamma=4$ J/mol K^2.[6] In this work we report a study of the physical properties of a member of the $M=$Co 3-4-13 series, $Gd_3Co_4Sn_{13}$. Along the rare-earth series, the Gd^{3+} ions are particularly interesting because they present *S* state ($S=7/2$, $L=0$) ground state for which the CEF effect is a high order effect. As such, along series of rare-earth-based intermetallic magnetic compounds, the Gd-based materials are taken as reference compounds where the magnetic materials purely reflect the details of RKKY magnetic interaction and Fermi surface effects.[7,8] Besides, the Gd^{3+} are excellent probes for electron spin resonance (ESR) experiment which can reveal details about the microscopic interaction J_{fs}, between the Gd^{3+} 4*f* electrons and the conduction-electrons (c-e). We have performed measurements of magnetic susceptibility, heat capacity, electrical resistivity, and ESR for single crystals of $Gd_3Co_4Sn_{13}$. This compound is a metallic Curie-Weiss paramagnet at high temperature that undergoes to an antiferromagnetically ordered state below $T_N=14.5$ K. In the paramagnetic state, the ESR experiments combined with the magnetic susceptibility and specific heat data for $Gd_3Co_4Sn_{13}$, allowed us to extract the exchange parameters between the Gd^{3+} local moments and the c-e in this compound, which was found to be c-e wave-vector independent.[9] From this data, we have also inferred that the electronic structure of $Gd_3Co_4Sn_{13}$ has a single band character.

II. EXPERIMENT

The single crystals of $Gd_3Co_4Sn_{13}$ were synthesized from a Sn-flux method.[5] The crystal structure and phase purity of this compound were determined by x-ray powder diffraction. It crystallizes with the $Yb_3M_4Sn_{13}$-type structure, space group Pm-3*n*, which has 40 atoms per unit cell, and the extracted cubic lattice parameters was 9.51 Å. The two Sn^1 atoms occupy the 2*a* (0,0,0) positions, the six rare-earth atoms the 6*d* (1/4,1/2,0) positions, the eight Co atoms the 8*e* (1/4,1/4,1/4) positions, and the 24 Sn^2 atoms the 24 000 (*Oyz*) positions. The ESR experiments were carried out in a conventional Bruker ESR spectrometer using a TE_{102} room-*T* cavity. The sample temperature was varied using a helium gas-flux temperature controller. Specific heat measurements were performed in a Quantum Design PPMS small-mass calorimeter that employs a quasiadiabatic thermal relaxation technique. Magnetization measurements were

[a)]Electronic mail: pagliuso@ifi.unicamp.br

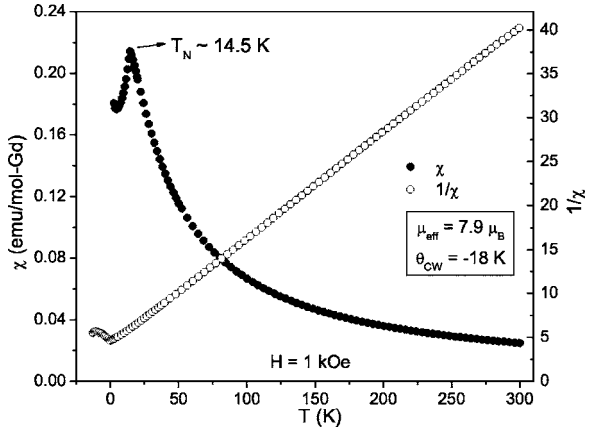

FIG. 1. Temperature dependence of the magnetic susceptibility and its inverse taken with an applied field $H=1$ kOe for the $Gd_3Co_4Sn_{13}$ intermetallic compound.

made in a Quantum Design dc superconducting quantum interference device and electrical resistivity was measured using the PPMS low-frequency ac resistance bridge and four-contact configuration. Fine powder of crushed single crystals were used in the ESR experiments in order to increase the ESR signal to noise ratio.

III. RESULTS AND DISCUSSION

The magnetic susceptibility (and the respective inverse) as a function of temperature measured at $H=1$ kOe for a single crystal of $Gd_3Co_4Sn_{13}$ is shown in Fig. 1. An antiferromagnetic (AFM) phase transition is observed at $T_N=14.5$ K. From the Curie-Weiss linear fits of the inverse of the magnetic susceptibility for $T>50$ K, we have extracted an effective moment $\mu_{\text{eff}}=7.9(2)\mu_B$ for Gd^{3+} in $Gd_3Co_4Sn_{13}$ in agreement with its theoretical value. A Curie-Weiss temperature $\theta_{\text{CW}}\approx -18$ K obtained from this fit reveals no sign of magnetic frustration.

Figure 2(a) presents the temperature dependence of the electrical resistivity measured in a single crystal of $Gd_3Co_4Sn_{13}$. A weak metallic-like behavior is observed in the paramagnetic regime and a clear kink can be noted at $T_N=14.5$ K. Interestingly, instead of the typical crossover to a more rapid (exponentially like) decreasing of the c-e magnetic scattering below T_N observed in the resistivity of AFM intermetallic materials,[7] the resistivity of $Gd_3Co_4Sn_{13}$ shows smaller $d\rho/dT$ below T_N. The specific heat per mole of Gd divided by temperature, and the corresponding magnetic entropy is displayed in panel 2(b) for the temperature range $2\text{ K}\lesssim T\lesssim 30$ K.

To calculate the magnetic entropy, the phonon contribution was estimated from the specific heat data of $La_3Co_4Sn_{13}$ (Ref. 5) and subtracted from the total specific heat of the $Gd_3Co_4Sn_{13}$ compound. A sharp main peak in C/T corresponding to the onset of AFM order can be seen at $T_N=14.5$ K in very good agreement with the temperature where the maximum in the magnetic susceptibility occurs (see Fig. 1). The magnetic entropy recovered at T_N roughly reaches the value of Rln8 expected for the whole Gd^{3+} $S=7/2$.

Figure 3(a) shows the ESR powder spectra measured at $T=60$ K and 3(b) the temperature dependence of the linewidth for Gd^{3+} in the $Gd_3Co_4Sn_{13}$ compound. In the paramagnetic state, the Dysonian[10] ESR line shapes characteristic of localized magnetic moments in a lattice with a skin depth smaller than the size of the sample particles were observed. The g-value and linewidth were obtained from the fitting of the resonances to the appropriate admixture of absorption and dispersion.[10] For $T\gtrsim 60$ K, a single nearly temperature independent $g\sim 2.005(2)$ is observed, and its linewidth follows a Korringa-like behavior as a function of temperature.

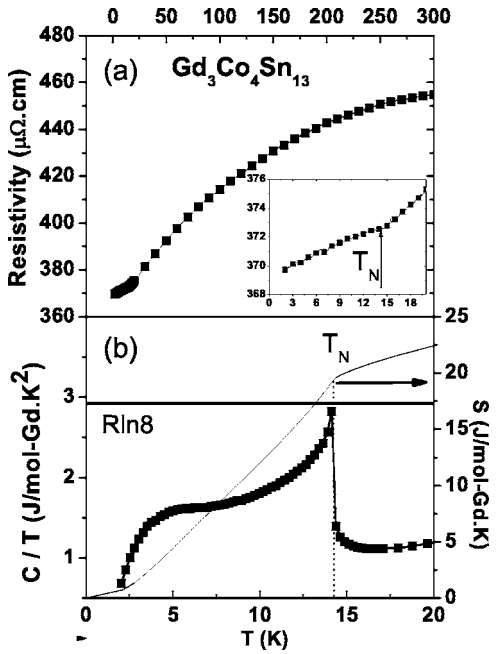

FIG. 2. (a) Temperature dependence of the electrical resistivity; (b) specific heat per mole of Gd divided by temperature as a function of temperature and the corresponding magnetic entropy for $Gd_3Co_4Sn_{13}$.

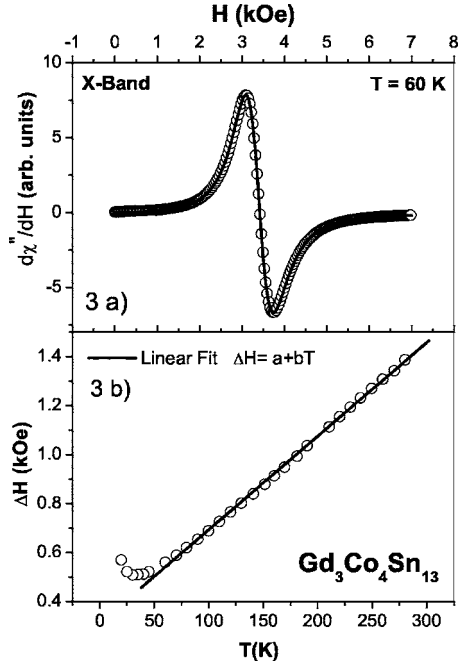

FIG. 3. (a) ESR powder spectra at $T=60$ K and (b) temperature dependence of the ESR linewidth for $Gd_3Co_4Sn_{13}$. The solid line is the best fit to $\Delta H=a+bT$, yielding $a=310(20)$ Oe and $b=3.8(4)$ Oe/K.

At much lower temperatures the ESR linewidth starts to broaden as a consequence of the development of short range magnetic correlation. The high-T linear dependence of the linewidth was fitted to the expression $\Delta H = a + bT$, with $a = 310(20)$ Oe and $b = 3.8(4)$ Oe/K for Gd^{3+} in $Gd_3Co_4Sn_{13}$. In single crystals of $Gd_3Co_4Sn_{13}$, the Gd^{3+} resonance did not show crystal field features, i.e., fine structure and/or anisotropic linewidth for any range of temperature.

In the simplest treatment of the exchange interaction, $J_{fs}\mathbf{S}\cdot\mathbf{s}$, between a localized $4f$ electron spin ($\mathbf{S}$) on a solute atom (Gd^{3+}) and the free c-e's spin ($\mathbf{s}$) of the host metal, the ESR g-shift (Knight shift)[11] and the thermal broadening of the linewidth (Korringa rate),[12] when *bottleneck* and *dynamic* effects are not present,[13] can be written as

$$\Delta g = J_{fs}\eta(E_F), \tag{1}$$

and

$$\frac{d(\Delta H)}{dT} = \frac{\pi k_B}{g\mu_B} J_{fs}^2 \eta^2(E_F), \tag{2}$$

where J_{fs} is the effective exchange interaction between the Gd^{3+} local moment and the c-e in the absence of c-e momentum transfer,[9] $\eta(E_F)$ the *bare* density of states for one spin direction at the Fermi surface, k_B is the Boltzmann constant, μ_B is the Bohr magneton, and g is the Gd^{3+} g-value.

Equations (1) and (2) are normally used in the analysis of ESR data for highly diluted rare-earths magnetic moments in intermetallic compounds with appreciable residual resistivity, i.e., large c-e spin-flip scattering. In these cases, it is expected that the following relation may hold

$$\frac{d(\Delta H)}{dT} = \frac{\pi k_B}{g\mu_B}(\Delta g)^2. \tag{3}$$

Using the g-value of Gd^{3+} in insulators as 1.993(2),[14] $(\pi k/g\mu_B) = 2.34 \times 10^4$ Oe/K, and the measured g-shift $\Delta g \approx 0.012(3)$ for the Gd^{3+} resonance in $Gd_3Co_4Sn_{13}$ a thermal broadening of $b \approx 3.5(2)$ Oe/K is obtained from Eq. (3). That value is, in fact, very close to the one measured, $b \approx 3.8(4)$ Oe/K. Therefore, we can conclude that the approximations made in Eqs. (1) and (2) are valid for this compound, and conduction electron-electron correlations,[15,16] $\mathbf{q}$-dependent of the exchange interaction, $J_{fs}(\mathbf{q})$,[9] and multiple band effects[17] do not need to be taken into account in the analysis of our ESR data.

Hence, in order to calculate the effective exchange interaction between the Gd^{3+} local moment and the c-e J_{fs} for $Gd_3Co_4Sn_{13}$ using Eqs. (1) and (2), one needs to estimate the bare density of states for one spin direction at the Fermi surface, $\eta(E_F)$ for $Gd_3Co_4Sn_{13}$. Within a free c-e gas model description $\eta(E_F)$ is related to the electronic contribution to the specific heat according to the expression $\gamma = (2/3)\pi k_B^2 \eta(E_F)$.

From Fig. 2(b) one can see that a nonobvious magnon contribution to the low-T specific heat of $Gd_3Co_4Sn_{13}$ difficult the correct estimation of γ from the specific heat of $Gd_3Co_4Sn_{13}$. As Gd^{3+} and La^{3+} are trivalent and both contributes with one $5d$ and two $6s$ electrons to the conduction band, we used the specific heat data of $La_3Co_4Sn_{13}$ (Ref. 5) to estimate a value for $\eta(E_F)$ for $Gd_3Co_4Sn_{13}$. An electronic specific heat $\gamma = 6(1)$ mJ/mol La K^2 for $La_3Co_4Sn_{13}$ (Ref. 5) yields $\eta(E_F) = 1.25(5)$ states/eV mol spin. For this density of states, one would expect an electronic spin susceptibility $\chi_e = 2\mu_B\eta(E_F) \approx 0.07 \times 10^{-3}$ emu/mol. That is of the order of the Pauli susceptibility (corrected for the core diamagnetism) measured for $La_3Co_4Sn_{13}$,[5] but cannot be appreciable in Fig. 1 due to the much stronger contribution of the Gd^{3+} magnetic susceptibility.

Using $\eta(E_F) = 1.25(5)$ states/eV mol spin and Eqs. (1) and (2), we calculated a $\mathbf{q}$-indepedent effective exchange interaction between Gd^{3+} local moments and the c-e, $J_{fs} = 10(2)$ meV. This value of $\mathbf{q}$-indepedent $J_{fs} = 10(2)$ meV and the single band character of the electronic structure of $Gd_3Co_4Sn_{13}$ may be useful in the study of the evolution of the magnetic properties and/or the HF behavior along the $R_3Co_4Sn_{13}$ series.[5,6,18]

IV. CONCLUSIONS

In summary, the experiments of magnetic susceptibility, heat capacity, electrical resistivity, and ESR revealed that the intermetallic compound $Gd_3Co_4Sn_{13}$ is a metallic Curie-Weiss paramagnet at high temperature and presents an antiferromagnetic ordering below $T_N = 14.5$ K. In the studies of ESR in the paramagnetic state, we have found a single Gd^{3+} ESR line with a nearly temperature independent $g \sim 2.005(2)$ and a Korringa-like behavior as a function of temperature for the ESR linewidth. From the obtained Korringa rate ($\Delta H/\Delta T \sim 4$ Oe/K) a g-shift ($\Delta g \sim 0.012$) we have extracted the exchange parameters between the Gd^{3+} local moments and the c-e in this compound. This exchange parameter $J_{fs} \approx 10$ meV was found to be c-e wave-vector independent and the electronic structure of $Gd_3Co_4Sn_{13}$ has a single band character of the Fermi surface.

ACKNOWLEDGMENTS

This work was supported by FAPESP-SP-Brazil and CNPq-Brazil.

[1] J. P. Remeika *et al.*, Solid State Commun. **34**, 923 (1980).
[2] J. P. Remeika *et al.*, Solid State Commun. **42**, 97 (1982).
[3] H. Sato *et al.*, Physica B **188**, 630 (1993).
[4] M. F. Hundley *et al.*, Phys. Rev. B **65**, 024401 (2002).
[5] C. Israel *et al.*, Physica B **359–361**, 251 (2005).
[6] A. Cornelius *et al.*, to appear in Physica B.
[7] P. G. Pagliuso *et al.*, Phys. Rev. B **63**, 054426 (2001).
[8] E. Granado *et al.*, Phys. Rev. B **69**, 144411 (2004).
[9] D. Davidov, K. Maki, R. Orbach, C. Rettori, and E. P. Chock, Solid State Commun. **12**, 621 (1973).
[10] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955); F. J. Dyson, *ibid.* **98**, 349 (1955).
[11] K. Yosida, Phys. Rev. **106**, 893 (1957).
[12] J. Korringa, Physica (Amsterdam) **16**, 601 (1950).
[13] C. Rettori, H. M. Kim, E. P. Chock, and D. Davidov, Phys. Rev. B **10**, 1826 (1974).
[14] A. Abragam and B. Bleaney, *EPR of Transition Ions* (Clarendon, Oxford, 1970).
[15] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).
[16] A. Narath, Phys. Rev. **163**, 232 (1967).
[17] P. G. Pagliuso *et al.*, Phys. Rev. B **60**, 13515 (1999).
[18] E. M. Bittar *et al.* (in preparation).