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Intermetallic solid solution $Fe_{1-x}Co_xGa_3$: Synthesis, structure, NQR study and electronic band structure calculations

V.Yu. Verchenko [a], M.S. Likhanov [a], M.A. Kirsanova [a], A.A Gippius [b,c], A.V. Tkachev [b,c], N.E. Gervits [b,c], A.V. Galeeva [b], N. Büttgen [d], W. Krätschmer [d], C.S. Lue [e], K.S. Okhotnikov [f], A.V. Shevelkov [a,*]

[a] *Department of Chemistry, Lomonosov Moscow State University, Moscow 119991, Russia*
[b] *Faculty of Physics, Lomonosov Moscow State University, Moscow 119991, Russia*
[c] *A.V. Shubnikov Institute of Crystallography, Moscow 119333, Russia*
[d] *Institut für Physik, University of Augsburg, Augsburg D-86135, Germany*
[e] *Department of Physics, National Cheng Kung University, Tainan 70101, Taiwan*
[f] *Materials and Environmental Chemistry, Stockholm University, Stockholm, Sweden*

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ABSTRACT

Unlimited solid solution $Fe_{1-x}Co_xGa_3$ was prepared from Ga flux. Its crystal structure was refined for $Fe_{0.5}Co_{0.5}Ga_3$ ($P4_2/mnm$, $a=6.2436(9)$, $c=6.4654(13)$, $Z=4$) and showed no ordering of the metal atoms. A combination of the electronic band structure calculations within the density functional theory (DFT) approach and ^{69,71}Ga nuclear quadrupole resonance (NQR) spectroscopy clearly shows that the Fe–Fe and Co–Co dumbbells are preferred to the Fe–Co dumbbells in the crystals structure. The band structure features a band gap of about 0.4 eV, with the Fermi level crossing peaks of a substantial density of electronic states above the gap for $x>0$. The solid solution is metallic for $x>0.025$. The study of the nuclear spin–lattice relaxation shows that the rate of the relaxation, $1/T_1$, is very sensitive to the Co concentration and correlates well with the square of the density of states at the Fermi level, $N^2(E_F)$.

1. Introduction

The overwhelming majority of intermetallic compounds behave as metals, and exceptions are rare. There exist a number of binary and ternary compounds that are semiconductors. They include several Heusler and half-Heusler compounds [1,2], $RuAl_2$ and $RuGa_2$ with the $TiSi_2$ structure type [3], and $FeGa_3$ [4]. In 2002, the latter was reported by Häussermann et al. to be an intermetallic semiconductor with the band gap of approximately 0.3 eV [4]. This affirmation was predicted by band structure calculations and proved by resistivity measurements carried out on a $FeGa_3$ single crystal. Opening of the narrow band gap in the case of $FeGa_3$ originates from the overlap of the Fe 3*d* and Ga 4*p* orbitals; thus, one can expect the same behavior in another intermetallic compounds containing both *d* and *p* metals. Transport properties of compounds with the $FeGa_3$ type of crystal structure, namely $CoGa_3$, $RuGa_3$, and $RuIn_3$, were investigated. As follows from the results of measurements, $RuGa_3$ [4] and $RuIn_3$ [5] show semiconductor-like behavior whereas $CoGa_3$ [4] is a metallic conductor. This indicates that not only a combination of elements leads to the formation of semiconductor properties but there is another crucial term, which is the number of valence electrons. For the compounds with 17 electrons per formula unit, namely $FeGa_3$, $RuGa_3$ and $RuIn_3$, band structure calculations confirm that the Fermi level locates in the band gap whereas for the 18 electron compounds the Fermi level shifts towards the conduction band, dividing nonbonding and antibonding states.

Recently $FeGa_3$ attracted attention as a potential thermoelectric material [6] and as a candidate for half-metallic ferromagnetism relevant for spintronic applications [7]. It was shown [7] that a few percent cobalt doping to intermetallic $FeGa_3$ drastically changes properties of the parent compound. Namely, the 5% Co doped specimen reveals itself as a bad metal and a Curie–Weiss paramagnet in contrast to semiconducting and nonmagnetic $FeGa_3$. Actually, the observed effect of doping on physical properties is connected with the creation of local magnetic moments and increase of valence electron concentration (VEC) in the parent compound. It appears from this that the number of valence electrons has an impact on transport and magnetic properties, and the substitution of Fe atoms by Co ones to a greater extent demands further investigation. Since both intermetallics $FeGa_3$ and $CoGa_3$ possess the same type of crystal

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[*] Corresponding author. Fax: +7 495 939 4788.
E-mail address: shev@inorg.chem.msu.ru (A.V. Shevelkov).

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structure we assumed the formation of the continuous solid solution between them. The solid solution with the formula $Fe_{1-x}Co_xGa_3$ would have an intermediate and controllable number of valence electrons, providing possibilities to study physical properties for different values of VEC. Besides the dependence of physical properties upon VEC, there is another crucial issue, which is the detailed characterization of the solid solution crystal structure depending on the content of cobalt. This issue includes the determination of interatomic distances and angles, and analysis of Fe and Co atoms crystallographic distribution. To this end, local features of the crystal and electronic structure can be probed by nuclear quadrupole resonance (NQR) spectroscopy, which is also proved to be a powerful tool for studying the distribution of electron density through measuring the rate of spin–lattice relaxation [8].

In this work we report on the synthesis, structure, and properties of the $Fe_{1-x}Co_xGa_3$ solid solution for $0<x<1$. In particular, we report on the crystal growth from Ga excess and on the non-Vegard behavior of this solid solution, present evidence on the metal atoms distribution obtained from a combination of the XRD and NQR study, discuss the evolution of its electronic structure with changing Co concentration, and present electrical conductivity for different x values.

2. Experimental section

2.1. Synthesis

The target solid solution $Fe_{1-x}Co_xGa_3$ was prepared from the elements: Fe powder (Acros Organics, 99%), Co powder (Alfa Aesar, 99.8%), and Ga rods (Aldrich, 99.999%). A series of $Fe_{1-x}Co_xGa_3$ specimens with $x=0$, 0.025, 0.125, 0.25, 0.375, 0.44, 0.5, 0.56, 0.625, 0.75, 0.875, 1 was synthesized. At first a thin layer of carbon was deposited on the inside of quartz ampoules by pyrolysis of acetone. Reactants with excess gallium (molar ratio M:Ga = 1:15, where M is the total quantity of Fe and Co, were loaded into the precarbonized ampoules, which were then sealed under vacuum at a pressure less than 10^{-2} Torr and placed into a programmable furnace. All samples were heated to 1123 K at the rate of 100 K/h, held at this temperature for 55 h to obtain a homogeneous melt, slowly cooled to 793 K at the rate of 4 K/h, and finally cooled to the ambient temperature in the shut off furnace. Excess of gallium metal was separated at 313 K in an Eppendorf 5804R centrifuge, yielding well-shaped silvery-gray crystals with a linear size up to 5 mm. The obtained crystals were purged from the remainder of Ga metal with diluted 0.5 M HCl and washed with distilled water and acetone.

2.2. X-ray diffraction

X-ray powder diffraction experiments were performed on a Stoe STADI-IP diffractometer with Cu$K_{\alpha 1}$ radiation (Ge monochromator, $\lambda_{Cu}=1.540598$ Å) by using Si as an internal standard ($a=5.43088$ Å). The crystals were finely ground and spread on a thick amorphous film. Unit cell parameters were calculated from least-squares fits using the standard program package Stoe WinXPOW.

For the crystal structure determination, a suitable single crystal with composition $Fe_{0.5}Co_{0.5}Ga_3$, which was confirmed by EDXS, was selected from the products of the synthesis and mounted on an IPDS II diffractometer (Stoe) equipped with a graphite monochromator, a Mo X-ray source ($\lambda_{Mo}=0.71073$ Å), and an image plate detector. The data collection nominally covered a full sphere of the reciprocal space. The data were corrected for Lorentzian polarization, extinction, and absorption (assuming a spherical crystal). The crystal structure was solved and refined against F^2 by using SHELX-97 programs. [9]. Details of the data collection and refinement are listed in Table 1. The crystal structure was solved and refined in the space group $P4_2/mnm$, pertinent to the $FeGa_3$ structure type and confirmed by the systematic extinction conditions. The refined atomic parameters are listed in Tables 2 and 3. As iron and cobalt atoms are not distinguishable by X-ray diffraction, the unique atomic position occupied by the metal atom was introduced as jointly populated by Fe and Co in a 1:1 ratio. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +(49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), reference number CSD-XXXXXX.

2.3. EDXS analysis

To determine the composition of the obtained samples, crystals were carefully crushed in an agate mortar. After this, fresh chips were investigated with a JSM JEOL scanning electron microscope operated at 30 kV and equipped with an EDX detection system INCA x-Sight. The data were collected from 10 points for each sample and then averaged. In all cases, pure elemental Co was used as a standard.

2.4. Thermal analysis

Simultaneous thermal analysis was performed using an STA 409 PC Luxx (Netzsch) thermobalance. The analysis was performed in fry argon flow up to 1273 K with a heating and cooling rate of 10 K min^{-1} and in air up to 1173 K with the same ramp

Table 1
X-ray single-crystal data collection and refinement parameters for $Fe_{0.5}Co_{0.5}Ga_3$.

Crystal system	Tetragonal
Space group	$P4_2/mnm$
Personal symbol	$tP16$
a [Å]	6.2436 (9)
c [Å]	6.4654 (13)
V [Å^3]	252.04 (12)
Z	4
ρ_{calcd} [g cm^{-3}]	7.025
μ [mm^{-1}]	37.38
$F(0\,0\,0)$	478
Max. 2θ [°]	58.19
hkl indices range	$-8 \le h \le 5$
	$-7 \le k \le 8$
	$-7 \le l \le 8$
Independent reflections	204
Reflections with $F_0 > 4\sigma(F_0)$	192
Parameters	15
Goodness-of-fit	1.20
R^1 $[F_0 > 4\sigma(F_0)]$	0.047
R^1/wR^2 (all)	0.051/0.122
Extinction coefficient	0.011 (4)

Table 2
Atomic parameters for the crystal structure of $Fe_{0.5}Co_{0.5}Ga_3$.

Atom	Wyckoff site	x	y	z	s.o.f.	U_{eq} [$\times 10^4$ Å^2]
M	$4f$	0.84566 (17)	$-x$	0	0.5Fe+0.5Co	77 (5)
Ga1	$4c$	0.5	0	0	1	177 (6)
Ga2	$8j$	0.15287 (15)	x	0.24366 (15)	1	163 (5)