STRONG EFFECT OF MULTIPLICITY FLUCTUATIONS IN RARE-EARTH COBALTITES ON MAGNETIC, ELECTRONIC, AND CRYSTAL STRUCTURE PROPERTIES

S.G. Ovchinnikov [1,a], V.A. Dudnikov [1,b], Yu.S.Orlov [1,c], M. V. Gorev[1,d]

[1] *Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, Russia*
[a] *sgo@iph.krasn.ru*, [b]*slad63@yandex.ru*, [c]*jso.krasn@mail.ru*, [d]*gorev@iph.krasn.ru*

Abstract. The perovskite compounds $ReCoO_{3-y}$ (Re is Nd, Sm, Gd) have a number of unusual magnetic, electronic, and lattice properties related to the temperature induce spin state crossover from the low spin (LS) to the high spin (HS) states of the Co^{+3} ions. We have synthesized high quality polycrystalline samples and have measured temperature dependence of the X-ray diffraction, magnetic susceptibility, and lattice dilatation. All observed anomalies are related to the smooth increase of the concentration of the HS ions that are excited over the spin gap between HS and LS terms. Spin gap itself decreases with lattice expansion and goes to zero at the spin crossover temperature. The spin gap is determined by the Re ionic radii.

1. Introduction

Anomalous magnetic, electronic and lattice properties of LaCoO3 and other rare-earth cobaltites are known for a long time. It is known that the ground state of the Co^{+3} ions is the LS, and magnetic properties are thermally induced by the increasing occupation of the HS ions. The excitation from LS to HS ionic terms (the multiplicity fluctuations) occurs via the spin gap, its value is small ~100K for La and increases going from La to Y. For Gd we have estimated this gap 2000K at zero temperature. Due to lattice dilatation with heating the gap is decreasing, and tends to zero at the spin crossover temperature T*. We have demonstrated this behavior earlier for GdCoO3 where T*=800K [1]. The aim of this work is to prepare and study the complex of physical properties of Nd and Sm cobaltites where smaller spin gap is expected and the spin crossover temperature may be decreased to more convenient values.

2. Experimental procedure and sample preparation

Polycrystalline ceramic samples of SmCoO3 and NdCoO3 were prepared from a stoichiometric compositions of high quality oxides Co3O4 , Sm2O3, and Nd2O3 that were carefully mixed and heated at 1473 K in air during 24 h. After the annealing, the mixture was reground, and the powder was pressed to form pellets in the shape of bricks $5 \times 10 \times 2$ mm^3. The pellets were annealed in air for 8 h at 1373 K, and then slowly cooled together with the furnace down to room temperature at the speed about 2 K/h.

Powder XRD patterns were recorded on a PANalytical X'Pert PRO diffractometer with a solid state detector PIXcel using Co Kα radiation. High temperature measurements were performed using an Anton Paar HTK 1200N stage.

The volume thermal expansion was measured in the temperature range 100−750 K with an induction dilatometer Netzsch DIL-402C calibrated with a silica glass as a standard in dynamic mode with heating and cooling rate 0.05 K/s in a flow of dry helium (O2 concentration is about 0.05% of volume).

Magnetic field and temperature dependences of magnetization in the temperature range 2−400 K were measured with the Physical Properties Measurement System (PPMS-9) by Quantum Design.

3. Experimental results

The XRD data has revealed single phase sample with the lattice parameters corresponding to the literature data. The experimental temperature dependences of the volumetric thermal expansion coefficient β, obtained in heating-cooling modes, do not show hysteresis differences and are shown in Fig. 1.

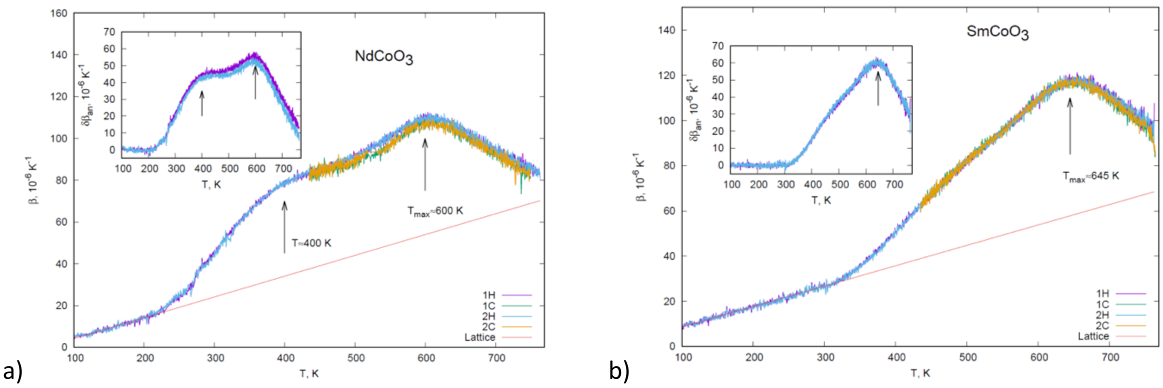

Fig. 1. Temperature dependences of the volumetric thermal expansion coefficient β for the samples ReCoO3 (Re = Nd (a), Sm(b)). The abnormal contributions to the thermal expansion coefficient are obtained by substracting linear contribution from the experimental values and are shown in the inset.

The high temperature maximum of the dilatation has been found earlier in LaCoO3, GdCoO3 and their solid solutions [2], it corresponds to the spin crossover temperature T*. It is larger in SmCoO3 vs NdCoO3 because zero temperature spin gap in SmCoO3 is ~1500K, while in NdCoO3 it is ~1000K [3]. The low temperature maximum for NdCoO3 corresponds to the maximal variation of HS concentration dn_{HS}/dT [2].For cobaltites with larger spin gap the maximal rate of the multiplicity fluctuations is achieved at higher temperatures and is close to T*. Similar two peak structure for NdCoO3 and single peak for SmCoO3 we have found in magnetic susceptibility temperature dependence.

Conclusions

The lattice dilatation with increasing temperature has the effect of the negative pressure that increases fluctuations of the multiplicity and results in the spin crossover of the LS state stable at low temperature into the HS state stable at high temperature. The average value of spin is temperature dependent, and reach its nominal for HS value S=2 only at temperature T>>T*. The physical origin of the strong deviations of the dilatation from the linear behavior is the large (about 10%) difference in the ionic radii of the LS and HS states of Co+3 ions. The characteristic spin crossover temperature T* is found to be 600K in NdCoO3, and 645K in SmCoO3.

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