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Abstract

Both differential scanning calorimetry and powder neutron diffraction have been applied to investigate an oxygen isotope effect on the metal–insulator (MI) transition in layered cobaltites RBaCo$_2$O$_{5.5}$ (R = Pr, Dy, Ho and Y). For all the compounds it was found that ^{18}O substitution increases the transition temperature T_{MI} by about 2 K. A small negative isotope-effect coefficient $\alpha_0 \sim -0.06$ indicates that a delocalization of the pdσ holes in the Co^{3+} high spin state (rather than a spin-state transition) can be responsible for the MI transition, in agreement with density-functional calculations (Wu 2003 *J. Phys.: Condens. Matter* **15** 503).

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The oxygen deficient layered double perovskites RBaCo$_2$O$_{5+\delta}$ (where R = rare earth element) are being increasingly studied because of their interesting magnetic and transport properties. In particular, the materials with $\delta = 0.5$ exhibit a metal–insulator (MI) as well as successive paramagnetic (PM) $\rightarrow$ ferromagnetic-like (FM) $\rightarrow$ antiferromagnetic (AFM) transitions, which are related to an interplay between spin, charge and orbital degrees of freedom of the cobalt ions [1–5]. In RBaCo$_2$O$_{5.5}$ ($\delta = 0.5$) only Co^{3+} ions are present, which are sited in ideally alternating octahedral CoO$_6$ and pyramidal CoO$_5$ environments. Depending on the ratio of the crystal field Δ_{cf} and the intra-atomic Δ_{ex} exchange energies, Co^{3+} ions can be stabilized either in low-spin (LS) state (t$_{2g}^6$e$_g^0$, $S = 0$), intermediate-spin (IS) state (t$_{2g}^5$e$_g^1$, $S = 1$) or high-spin (HS) state (t$_{2g}^4$e$_g^2$, $S = 2$). The IS state of Co^{3+} leads to a Jahn–Teller (JT) distortion

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of the oxygen octahedra in the structure[4]. It was shown in the past that perovskites containing JT cations show oxygen isotope effects (OIEs) on many physical properties. These were intensively studied in the case of superconducting cuprates (see e.g. [6, 7] for reviews) but also for giant magnetoresistive (GMR) manganates [8] and nickelates [9]. For both manganates and nickelates large (up to 20 K) OIEs have been found on the Curie temperature T_C and the MI transition temperature T_{MI}, respectively. All these experiments strongly suggest that lattice vibrations play an important role for many properties of the perovskites such as superconductivity, GMR and MI transition.

Layered cobaltites $RBaCo_2O_{5.5}$, similar to nickelates, show MI transitions in the temperature range 300 K $< T_{MI} <$ 340 K (depending on R), which is accompanied by a lattice distortion [1–5, 10–14]. The driving mechanism for the transition as well as the Co^{3+} spin state in both metal and insulator state remains controversial. In fact, all possible spin states have been claimed from neutron diffraction [4, 15, 16], synchrotron x-ray [10], spectroscopic [17, 18] and thermodynamic [4, 12, 13, 19] measurements as well as from band structure calculations [20–22]. Studies performed on $YBaCo_2O_{5.5}$ have shown that T_{MI} coincides with $T_{PM−FM}$ [14]. On the other hand, in $RBaCo_2O_{5.5}$ with R = Tb, Gd, Ho T_{MI} is remarkably higher than $T_{PM−FM}$ [4, 11, 23, 24]. Thus, it is difficult to conclude if a correlation between these two transitions exists. A similar situation was previously observed in nickelates where $T_{MI} \neq T_N$ (Néel temperature) [25]. Consequently, it was concluded that the MI transition in nickelates is not of magnetic origin [9]. Additionally, observations of a large OIE on T_{MI} suggested an existence of Jahn–Teller polarons narrowing the conduction bandwidth [26]. This narrowing is more pronounced for the heavier oxygen isotope, leading to an experimentally stated increase of T_{MI} [9]. If a similar polaronic picture is valid for cobaltites the MI transition should also be influenced by the oxygen isotope doping. Until now, however, no studies concerning the oxygen isotope effect in the case of cobaltites have been reported.

In this work differential scanning calorimetry (DSC) measurements have been performed for selected $RBaCo_2O_{5.5}$ samples substituted with ^{16}O- and ^{18}O-isotopes and oxygen contents close to $5 + \delta = 5.5$. They, together with some structural data, taken from neutron powder diffraction (NPD) on $HoBaCo_2O_{5.48}$, have permitted us to detect unambiguously the oxygen isotope effect on MI transition in this layered double-perovskite family.

2. Experiment

The samples $RBaCo_2O_{5+\delta}$ (R = Pr, Dy, Ho and Y) were synthesized by a solid state reaction using rare earth oxides, $BaCO_3$ and Co_3O_4 of a minimum purity of 99.99%. The respective amounts of starting reagents were mixed and calcined at temperatures of 1000–1150 °C for at least 100 h in air, with several intermediate grindings. The last annealing was performed in oxygen flow at 1050 °C (20 h) with slow 60 °C h^{-1} cooling. Oxygen exchange was performed using an experimental set-up as shown previously [27]. In order to ensure the same oxygen content for both ^{16}O- and ^{18}O-substituted samples, simultaneous annealing was performed in separate chambers (in $^{16}O_2$ and $^{18}O_2$ gas, respectively) at the same temperature and oxygen pressure (1.2±0.02 bar). The exchange was performed at 600 °C for several hours, followed by cooling with a rate 100 °C h^{-1} down to 450 °C and further 15 °C h^{-1} down to room temperature. Isotope ^{18}O content in the samples could be measured *in situ* using mass spectrometry and then after the exchange evaluating the weight enlargement of the sample. Additionally, thermogravimetry was used to measure ^{18}O content in the samples after a back-exchange

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[4] Note that the HS state is also JT active, since it has one electron in the t_{2g} spin down shell. However, the JT effect for the t_{2g} orbitals is much smaller than for the e_g orbitals. The LS state is not JT active.

with natural oxygen (99.8% isotope ^{16}O). For all our ^{18}O samples the isotope content was larger than 85%. For YBaCo$_2$O$_{5+\delta}$, DyBaCo$_2$O$_{5+\delta}$ and HoBaCo$_2$O$_{5+\delta}$, after oxygen exchange $\delta = 0.49$, 0.54 and 0.48 respectively have been determined by iodometry with an accuracy of ± 0.01 [28]. All these values are very close to 0.5, at which a strong MI transition has been reported. For PrBaCo$_2$O$_{5+\delta}$ a larger oxygen content $\delta = 0.81$ has been found. Therefore, the last samples (both ^{16}O and ^{18}O substituted) had to be reduced to $\delta = 0.5$ before the measurements. Our previous experiments showed that the best method is equilibration of the samples in closed ampoules with an appropriate amount of copper powder (getter substance) which reacts with oxygen [29, 30]. Thus, for each sample (^{16}O and ^{18}O substituted) an alumina crucible with powdered sample of exactly known weight and oxygen stoichiometry was placed in a quartz ampoule together with an exactly weighed copper powder in another crucible. The ampoule was then sealed under vacuum and heated up to 850 °C for 10 h followed by a slow cooling (5 °C h^{-1}) in order to ensure a homogenous oxygen distribution. Additionally to this, a series of ^{16}O samples with different oxygen contents within the range $0.4 < \delta < 0.6$ has been prepared in order to investigate a possible influence of the oxygen stoichiometry on the MI transition temperature. For all the samples phase purity was checked with a conventional x-ray diffractometer (Siemens D500).

Differential scanning calorimetry (DSC, Netzsch DSC 204F1) was used in this work, as it has been shown in the past [9, 14] that strong DSC peaks are observed at the metal–insulator transition. DSC experiments were performed during heating with a rate of 10 K min^{-1} using 30 mg powder samples encapsulated in standard Al crucibles. An argon stream was used during the whole experiment as protecting gas.

Neutron powder diffraction experiments were carried out at the SINQ spallation source of the Paul Scherrer Institute (Switzerland). The crystal structures of the samples were determined from the data taken with the high-resolution HRPT diffractometer [31] with the neutron wavelength $\lambda = 1.49$ Å. The refinements of the crystal and magnetic structure parameters were carried out with the FULLPROF [32] program.

3. Results

Layered RBaCo$_2$O$_{5.5}$ cobaltites are strongly oxygen nonstoichiometric compounds. Therefore, to measure the oxygen isotope effects, one has to be sure that the oxygen stoichiometries are equal within a pair of the substituted samples. Chemical methods of analysis are not always precise enough to rule out possible doubts. Therefore, it is extremely important to know to what extent oxygen content can influence the physical property assumed to be affected by the oxygen isotope substitution.

Figure 1 shows the DSC signal taken from PrBaCo$_2$O$_{5+\delta}$ samples with oxygen stoichiometries $0.4 \leqslant \delta \leqslant 0.55$. The measurements reveal a sharp transition which corresponds to the MI transition (compare e.g. [4, 14]). Note that another high-temperature structural transition was observed at $T \sim 770$ K (see inset in figure 1), whose origin was investigated by high resolution neutron diffraction and will be discussed elsewhere [33].

Figure 2 shows quantitatively oxygen content dependence of the MI transition temperature (DSC peak position) and heat of the transition (DSC peak area). It has to be noted that unless the absolute oxygen determination error of the iodometric titration is about ± 0.01, the relative (sample to sample) error of the oxygen content in the series is much smaller. This is because the oxygen content for the samples in the investigated series depends on the amount of the getter, which can be very precisely weighted. It is evident from figure 2 that around $\delta = 0.50$ for $\Delta\delta = 0.01$ (uncertainty of the iodometry) a 2–3 K shift of the MI transition temperature can be expected. This should be, however, accompanied by a simultaneous change of the
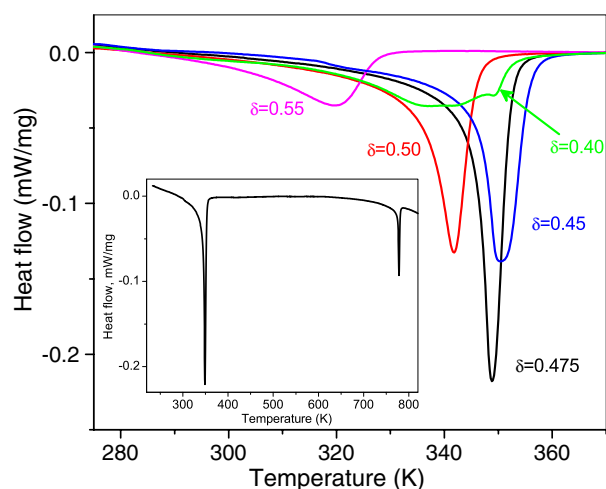
Figure 1. DSC measurements of the metal–insulator transition for $PrBaCo_2O_{5+\delta}$ samples with different δ values. The inset shows the temperature dependence $250\ K < T < 800\ K$ of the DSC signal taken from $PrBaCo_2O_{5.475}$. Additionally to the metal–insulator transition, the second, high-temperature transition is clearly observed.
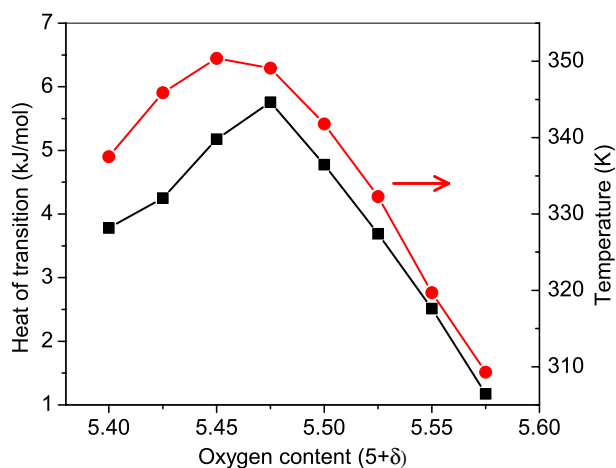

Figure 2. DSC measurements of peak temperatures (circles) and heat transitions (squares) at metal–insulator transition for $PrBaCo_2O_{5+\delta}$ samples with different δ values. The lines are guides to eyes.

transition heat of about 0.4 kJ mol^{-1}. As the transition heat can be measured by DSC with much higher precision, a possible discrepancy in the transition heat for ^{16}O- and ^{18}O-sample pairs can be used as a measure of inequality in oxygen content.

Table 1 and figures 3(a)–(d) summarize the results of the DSC measurements for four pairs of the ^{16}O and ^{18}O substituted $RBaCo_2O_{5+\delta}$ samples with different rare earth cations. The table shows average results together with standard deviations calculated from the results of three to five measurements. For all the pairs of substituted samples, pronounced shifts of the transition temperatures T_{MI} have been stated. We are convinced that these shifts do not originate from an oxygen content inequality as the relevant transition heats for ^{16}O and ^{18}O samples
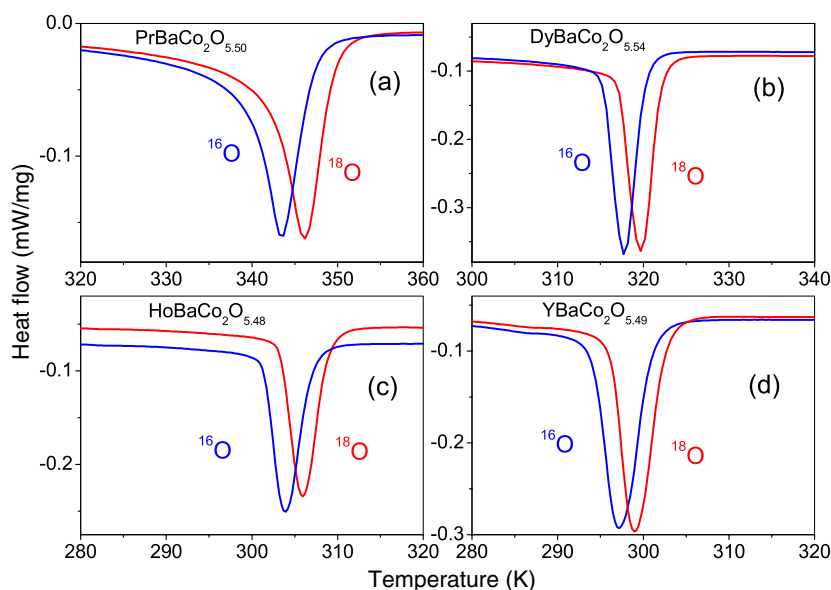
Figure 3. DSC measurements for ^{16}O and ^{18}O substituted RBaCo$_2$O$_{5+\delta}$ samples.

Table 1. Results of DSC study of RBaCo$_2$O$_{5+\delta}$ samples substituted with ^{16}O and ^{18}O.

	^{16}O		^{18}O	
Sample	Peak temp. (K)	Heat (kJ mol^{-1})	Peak temp. (K)	Heat (kJ mol^{-1})
PrBaCo$_2$O$_{5.50}$	343.6(4)	4.93(12)	345.9(3)	4.90(7)
DyBaCo$_2$O$_{5.54}$	317.9(2)	3.57(6)	319.6(1)	3.67(6)
HoBaCo$_2$O$_{5.48}$	303.8(1)	4.48(13)	306.0(1)	4.50(5)
YBaCo$_2$O$_{5.49}$	297.1(3)	2.89(11)	299.1(3)	2.74(13)

are identical within the measurement errors. The temperature shift observed for the metal–insulator transition ($\sim$2–3 K) substantially exceeds the uncertainty of the measurements, and therefore we conclude that the MI transition temperature is affected by the isotope substitution.

Since an MI transition is accompanied by a jump of the lattice parameters [4, 10], the high resolution neutron diffraction technique could be used as a complementary proof of the OIE in the layered cobaltites. The temperature dependences of the lattice parameters have been measured for both ^{16}O- and ^{18}O-substituted HoBaCo$_2$O$_{5.48}$ samples across the MI transition. The evolution of the cell parameters is shown in figure 4. An anisotropic change of the cell parameters and a sudden increase of the orthorhombic strain can be clearly seen. An oxygen isotope effect of about 2 K was detected, which is in excellent agreement with our DSC measurements. Detailed analysis of the evolution of the CoO$_6$ octahedra and the CoO$_5$ pyramids across the MI transition will be presented elsewhere [34].

4. Discussion

The performed experiments clearly show that the electronic properties of the studied compounds are influenced by the lattice vibrations. Let us discuss two important results
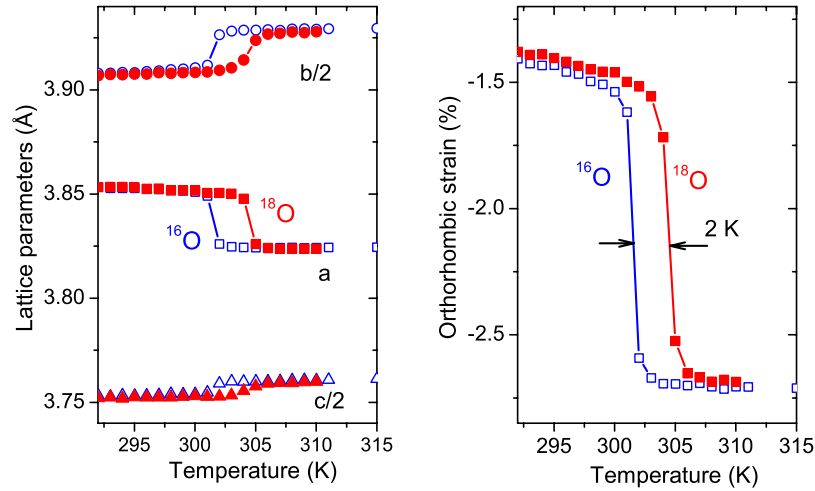
Figure 4. Lattice parameters and orthorhombic strain $((a - b)/(a + b) \cdot 200)$ for ^{16}O and ^{18}O substituted HoBaCo$_2$O$_{5.48}$ samples.

of our measurements, namely, (i) ^{18}O substitution increases the transition temperature T_{MI}; (ii) the OIE is rather weak compared to that in manganates and nickelates.

The effect of oxygen isotope substitution can be generally described by an isotope-effect exponent $\alpha_0 = -d \ln T_{MI}/d \ln m_0$, where m_0 is the O isotope mass. The absolute value of $\alpha_0 = -0.06(1)$ obtained for layered cobaltites in this work is much smaller than those measured for La$_{1-x}$Ca$_x$MnO$_{3+y}$ ($\alpha_0 \sim 0.8$) [8] and RNiO$_3$ ($\alpha_0 \sim -0.85$) [9]. The opposite sign of the isotope shift for manganates and nickelates was qualitatively explained using the JT polaron model [9]. According to this model, the gap energy $E_g \sim k_B T_{MI}$ of a charge-transfer (CT) insulator can be expressed as a difference between the charge-transfer energy Δ_{CT} and half of the bandwidth W, i.e., $k_B T_{MI} = \Delta_{CT} - W/2$. The JT polaron reduces the bandwidth by means of an exponential renormalization factor $W = W_b \exp(-\gamma E_{jt}/\hbar\omega)$, where E_{jt} is the JT energy and ω is the frequency of the active JT mode [35, 36]. In view of the fact that ω is inversely proportional to $\sqrt{m_0}$, one can expect a rise of T_{MI} by increasing the O isotope mass. On the other hand, the Curie temperature T_C of the hole-doped manganites is proportional to W, thus the opposite effect is expected. Since RBaCo$_2$O$_{5.5}$ can be classified as a pd CT oxide, the negative sign of α_0 is in agreement with this model.

Possible Co spin-state changes accompanying the MI transition require further clarification. It was suggested first that upon decreasing T across T_{MI} the Co^{3+} ions undergo a spin-state transition from an HS to an IS orbital-ordered (OO) state in both octahedra and pyramids [4]. Another model implies that the driving force for the MI transition is an HS → LS state transition of the Co^{3+} ions located in the octahedra, while the Co^{3+} ions in the pyramids keep their IS state [10]. However, using soft x-ray absorption spectroscopy Hu with co-workers [17] clearly demonstrated that pyramidal Co^{3+} ions are in an HS state. The effective magnetic moment as extracted from the high temperature Curie–Weiss behaviour also indicates an HS state for all Co^{3+} [1, 3]. Moreover, contrary to the common suggestion that only the IS state is JT active and can couple with the lattice distortion (see, i.e., [5]), weak octahedral/pyramidal distortions in cobaltites [4, 10] can be related to JT effect for the t$_{2g}$ orbitals in an HS state. This can explain the fact that the OIE observed in cobaltites is much smaller than that in manganates and nickelates.

By means of density-functional theory calculations it has been found that an MI transition can take place for the (almost) HS state of Co^{3+} due to a delocalization of the pdσ holes in the Co^{3+} HS state [22]. Simultaneous electron transfer gives rise to the experimentally observed lattice anomaly at T_{MI}. Recent resistivity measurements under pressure $p = 2.6$ GPa on TbBaCo$_2$O$_{5.5}$ reveal rather a small (<1 K GPa^{-1}) pressure coefficient of T_{MI} [37], also suggesting a weak change of the spin states at the MI transition. Thus, we suppose that the small negative isotope-effect coefficient α_0 supports the hole delocalization in the Co^{3+} HS state as a cause for the MI transition in layered cobaltites.

5. Conclusions

Differential scanning calorimetry proved to be a very powerful method in detecting MI transitions in the oxygen deficient layered double perovskites RBaCo$_2$O$_{5+\delta}$. We found for the first time that the transition temperature T_{MI} is increased by about 2 K ($\alpha_0 \sim -0.06$) upon ^{16}O $\rightarrow$ ^{18}O substitution. Moreover, our results suggest that the observed MI transition is due to hole delocalization in the Co^{3+} HS state, rather than a spin-state transition, in agreement with recent density-functional theory calculations [22].

Acknowledgments

References

[1] Martin C, Maignan A, Pelloquin D, Nguyen N and Raveau B 1997 *Appl. Phys. Lett.* **71** 1421
[2] Troyanchuk I O, Kasper N V, Khalyavin D D, Szymczak H, Szymczak R and Baran M 1998 *Phys. Rev. Lett.* **80** 3380
[3] Maignan A, Martin C, Pelloquin D, Nguyen N and Raveau B 1999 *J. Solid State Chem.* **142** 247
[4] Moritomo Y, Akimoto T, Takeo M, Machida A, Nishibori E, Takata M, Sakata M, Ohoyama K and Nakamura A 2000 *Phys. Rev.* B **61** R13325
[5] Kusuya H, Machida A, Moritomo Y, Kato K, Nishibori E, Takata M, Sakata M and Nakamura A 2001 *J. Phys. Soc. Japan* **70** 3577
[6] Franck J P, Hnatiw A, Yu M K, Cygax S, Soerensen G, Altendorf E and Irwin J C 1992 *Lattice Effects in High-T$_C$ Superconductors* (Singapore: World Scientific)
[7] Zhao G-M, Keller H and Conder K 2001 *J. Phys.: Condens. Matter* **13** R569
[8] Zhao G-M, Conder K, Keller H and Müller K A 1996 *Nature* **381** 676
[9] Medarde M, Lacorre P, Conder K, Fauth F and Furrer A 1998 *Phys. Rev. Lett.* **80** 2397
[10] Frontera C, García-Muñoz J L, Llobet A and Aranda M A G 2002 *Phys. Rev.* B **65** R180405
[11] Khalyavin D D, Barilo S N, Shiryaev S V, Bychkov G L, Troyanchuk I O, Furrer A, Allenspach P, Szymczak H and Szymczak R 2003 *Phys. Rev.* B **67** 214421
[12] Taskin A A, Lavrov A N and Ando Y 2003 *Phys. Rev. Lett.* **90** 227201
[13] Maignan A, Caignaert V, Raveau B, Khomskii D and Sawatzky G 2004 *Phys. Rev. Lett.* **93** 026401
[14] Akahoshi D and Ueda Y 2001 *J. Solid State Chem.* **156** 355
[15] Fauth F, Suard E, Caignaert V and Mirebeau I 2002 *Phys. Rev.* B **66** 184421
[16] Plakhty V P, Chernenkov Yu P, Barilo S N, Podlesnyak A, Pomjakushina E, Moskvin E V and Gavrilov S V 2005 *Phys. Rev.* B **71** 214407
[17] Hu Z, Hua Wu, Haverkort M W, Hsieh H H, Lin H-J, Lorenz T, Baier J, Reichl A, Bonn I, Felser Tanaka A, Chen C T and Tjeng L H 2004 *Phys. Rev. Lett.* **92** 207402
[18] Flavell W R, Thomas A G, Tsoutsou D, Mallick A K, North M, Seddon E A, Cacho C, Malins A E R, Patel S, Stockbauer R L, Kurtz R L, Sprunger P T, Barilo S N, Shiryaev S V and Bychkov G L 2004 *Phys. Rev.* B **70** 224427

[19] Zhou Z X and Schlottmann P 2005 *Phys. Rev.* B **71** 174401
[20] Wang J, Zhang W and Xing D Y 2001 *Phys. Rev.* B **64** 064418
[21] Kwon S K, Park J H and Min B I 2000 *Phys. Rev.* B **62** R14637
[22] Wu H 2000 *Phys. Rev.* B **62** R11953
     Wu H 2001 *Phys. Rev.* B **64** 092413
     Wu H 2002 *Eur. Phys. J.* B **30** 501
     Wu H 2003 *J. Phys.: Condens. Matter* **15** 503
[23] Respaud M, Frontera C, García-Muñoz J L, Aranda M A G, Raquet B, Broto J M, Rakoto H, Goiran M,
     Llobet A and Rodríguez-Carvajal J 2001 *Phys. Rev.* B **64** 214401
[24] Frontera C, García-Muñoz J L, Llobet A, Aranda M A G, Rodríguez-Carvajal J, Respaud M, Broto J M, Raquet B,
     Rakoto H and Goiran M 2002 *J. Magn. Magn. Mater.* **242–245** 751
[25] Rodríguez-Carvajal J, Rosenkranz S, Medarde M, Lacorre P, Fernandez-Díaz M T, Fauth F and Trounov V 1998
     Phys. Rev. B **57** 456
[26] Zhao G-M, Hunt M B, Keller H and Müller K A 1997 *Nature* **385** 236
[27] Conder K 2001 *Mater. Sci. Eng.* R **32** 41
[28] Conder K, Pomjakushina E, Soldatov A and Mitberg E 2005 *Mater. Res. Bull.* **40** 257
[29] Streule S, Podlesnyak A, Mesot J, Medarde M, Conder K, Pomjakushina E, Mitberg E and Kozhevnikov V 2005
     J. Phys.: Condens. Matter **17** 3317
[30] Podlesnyak A, Streule S, Medarde M, Conder K, Pomjakushina E and Mesot J 2005 *Physica* B **359–361** 1348
[31] Fischer P, Frey G, Koch M, Könnecke M, Pomjakushin V, Schefer J, Thut R, Schlumpf N, Bürge R, Greuter U,
     Bondt S and Berruyer E 2000 *Physica* B **276–278** 146
[32] Rodríguez-Carvajal J 1993 *Physica* B **192** 55
[33] Streule S, Podlesnyak A, Sheptyakov D, Mesot J, Pomjakushina E, Conder K, Stingaciu M and Medarde M
     J. Phys.: Condens. Matter at press
[34] Pomjakushina E, Conder K and Pomjakushin V 2005 at press
[35] Holstein T 1959 *Ann. Phys.* **8** 325
[36] Sturge M D 1967 *Solid State Physics: Advances in Research and Application* vol 20, ed D T F Seitz and
     H Eherenreich (New York: Academic) p 91
[37] Podlesnyak A, Streule S, Conder K, Pomjakushina E, Mesot J, Mirmelstein A, Schutzendorf P, Lengsdorf R and
     Abd-Elmeguid M M 2005 *Physica* B at press