

The spin states of cobalt ions and thermo-e.m.f. in erbium and holmium cobaltites

V.F.Khirnyi, A.A.Kozlovskii, A.V.Semenov, V.M.Puzikov

Institute for Single Crystals, STC "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Lenin Ave., 61001 Kharkiv, Ukraine

Received March 15, 2009

The temperature dependences of thermo-e.m.f. for $\text{Er}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, $\text{Er}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$, $\text{Ho}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ceramics have been studied in the temperature range of 300 K (of 100 K for some materials) to 600 K. The Zeebeck coefficient for Sr doped samples is lowered as the strontium content increases and the temperature rises. It has been shown that the $3d$ level splitting and the charge disproportionation of cobalt ions is to be taken into account to explain the above-mentioned behavior.

Исследованы температурные зависимости термо-ЭДС керамик $\text{Er}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, $\text{Er}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$, $\text{Ho}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ в области температур от 300 К (для некоторых от 100 К) до 600 К. Коэффициент Зеебека Sr-легированных образцов понижается при увеличении содержания стронция и температуры. Показано, что для объяснения такого поведения необходимо учитывать расщепление $3d$ -уровней и зарядовую диспропорционализацию ионов кобальта.

The correlation of electric charge carriers with spin and lattice excitations influences the electron properties of the perovskite structure ABO_3 compounds including high-temperature superconductors (HTSC), manganites and cobaltites. Each such compound is characterized by its unique features: HTSC, by high critical temperatures and magnetic fields; manganites, by colossal magnetoresistance; and cobaltites, by high thermo-e.m.f. values. At present, this is just the La–Sr–Co–O system compounds that are today the best studied among the cobaltites. So, for example, the Seebeck coefficient S value for $\text{La}_{0.95}\text{Sr}_{0.05}\text{CoO}_3$ is 710 $\mu\text{V}/\text{K}$ [1]. The cobaltites of other rare-earth elements are studied much lesser. The kinetic properties of perovskite type metal oxides are believed to be defined by the mean radius $\langle r_A \rangle$ of the cation in the A site [2].

In this work, studied are the thermoelectric properties of $\text{RECoO}_{3-\delta}$ (RE = Ho, Er) cobaltites doped with alkali-earth elements Sr and Ca. The ionic radii of holmium (0.901 Å)

and erbium (0.89 Å) are considerably smaller than that of lanthanum (1.032 Å) [3].

The $\text{Er}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, $\text{Er}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ and $\text{Ho}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ ceramics with $x = 0.15; 0.25; 0.35; 0.45; 0.55; 0.65; 0.75; 0.85; 0.95$ were synthesized by the standard solid phase technique. The samples obtained were shaped as rectangular parallelepipeds of $0.25 \times 0.55 \times 2.5 \text{ cm}^3$ size [4]. The synthesized ceramics were single-phase ones as determined by XPA carried out using a DRON-50 unit with $\text{CuK}\alpha$ emission. A typical XRD pattern is shown in Fig. 1. The Seebeck coefficient was determined by integral method with respect to copper. The contacts to the samples were realized by ultrasonic soldering of ultra-pure indium. The temperature gradient along the sample was measured using two chromel/alumel thermocouples (at $T \geq 300 \text{ K}$) or copper/constantan ones (at $T \leq 300 \text{ K}$). The control thermo-e.m.f. values were measured on a pure cobalt sample identical in size to the samples under study.

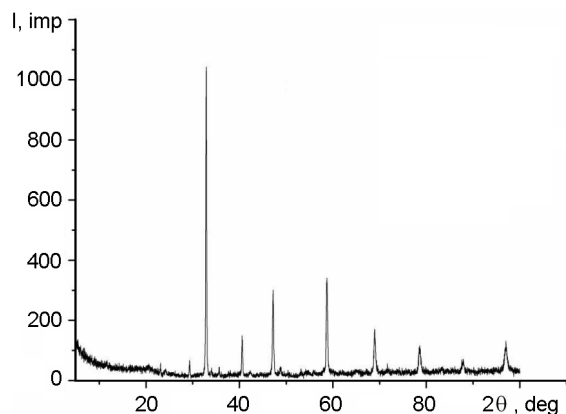


Fig. 1. XRD pattern of a $\text{Er}_{0.15}\text{Sr}_{0.85}\text{CoO}_{3-\delta}$ sample.

In Figs. 2 and 3, presented are the temperature dependences of Seebeck coefficient $S(T)$ for $\text{Er}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ and $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ceramics, respectively. (For $x = 0.15$ and $x = 0.25$ samples, the specific thermo-e.m.f. was temperature-independent). The measurements were carried out in the temperature range of 300 K (100 K for some samples) to $T \approx 600$ K. The S value decreased as the temperature rised, the holes being the major electric charge carriers, except for samples with $x = 0.95$ where the thermo-e.m.f. sign corresponded to the electron conductivity type at temperatures exceeding the room one.

To explaining the $S(T)$ decrease, it is to take into account that the $\text{RECoO}_{3-\delta}$ compounds are nonmagnetic dielectrics where the trivalent cobalt ions at low temperatures are in the low-spin (LS) Co^{III} diamagnetic state (spin $s = 0$) with $t_{2g}^6 e_g^0$ electron configuration. As the temperature rises, the Co^{III} LS state occupancy decreases due to thermal fluctuations (e.g. in LaCoO_3 at 100 K) and high-spin (HS) trivalent Co^{3+} ions appear with $t_{2g}^4 e_g^2$ and $s = 2$ [5]. In so doing, the electrons from the π band that is associated with localized t_{2g} orbitals pass to delocalized σ band formed by e_g orbitals. The temperature variation of $\text{Co}^{3+}/\text{Co}^{\text{III}}$ concentration ratio can be expressed [6] as

$$\text{Co}^{3+}/\text{Co}^{\text{III}} = \exp(-\Delta/k_B T), \quad (1)$$

where Δ is the energy difference between the ground low-spin state and the excited high-spin one; k_B , the Boltzmann constant. $\Delta = 2.04$ eV for HoCoO_3 [5].

At the substitution of Ho^{3+} and Er^{3+} by Sr^{2+} and Ca^{2+} , the Co ions are transformed into the mixed electron state $\text{Co}^{3+}/\text{Co}^{4+}$,

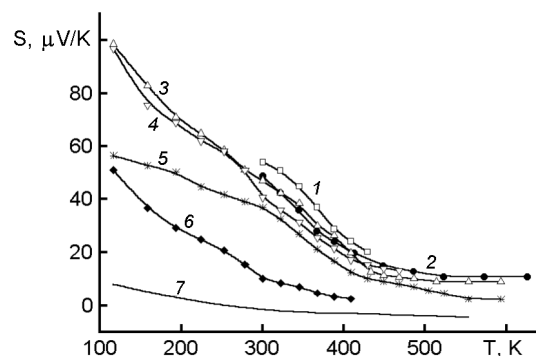


Fig. 2. Temperature dependences of Seebeck coefficient for the $\text{Er}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ system: $x=0.35$ (1); $x=0.45$ (2); $x=0.55$ (3); $x=0.65$ (4); $x=0.75$ (5); $x=0.85$ (6); $x=0.95$ (7).

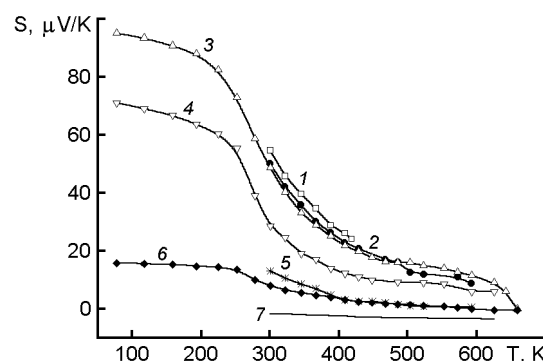


Fig. 3. Temperature dependences of Seebeck coefficient for the $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ system: $x=0.35$ (1); $x=0.45$ (2); $x=0.55$ (3); $x=0.65$ (4); $x=0.75$ (5); $x=0.85$ (6); $x=0.95$ (7).

taking into account the principle of electrical neutrality conservation. At the Co^{4+} ions, the mobile (delocalized) electric charge carriers are situated, thus causing an increased conductivity [7]. To explain that phenomenon, various models were used taking into account both the cation valency change [8] and the spin state distribution of cobalt ions resulting from the charge carrier disproportionation reaction [9].

For Sr doped samples, the temperature dependence of the Seebeck coefficient cannot be explained using the formula [8]

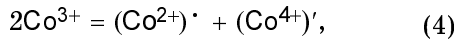
$$S = -(k_B/e) \ln[\text{Co}^{4+}/\text{Co}^{3+}], \quad (2)$$

where e is the elementary charge, assuming the cobaltites to be systems with mixed valence cations $\text{M}^{n+}/\text{M}^{n+1}$ and taking out of consideration the spin states. That is why let the modified Heikes formula be used where not only the spin states of cobalt ions

are considered but also the number of degenerated configurations thereof [16]:

$$S = -(k_B/e)\ln[(g_3/g_4)(x/(1-x))], \quad (3)$$

where g_3 and g_4 are the number of degenerated configurations for spin states of Co^{3+} and Co^{4+} ions, respectively; $x = \text{Co}^{4+}/\text{Co}$, the number of Co sites occupied by Co^{4+} ions. It is to take into account that as the temperature rises, the charge disproportionation reaction runs in the samples that is observed in most transition metal oxides with partially occupied $3d$ electron sublevels [7], such as Mn^{3+} ($t_{2g}^3e_g^1$) in $(\text{La,Ca})\text{MnO}_3$ [10, 11]; Mn_3O_4 [12], and $(\text{Y,Ca})\text{MnO}_3$ [10]; Fe^{4+} ($t_{2g}^3e_g^1$) in CaFeO_3 [13] and $\text{Sr}_{1-x}\text{La}_x\text{FeO}_3$ [14], as well as V^{4+} (t_{2g}^1) in $\text{La}_2\text{V}_2\text{O}_7$ [15]. Since the $\text{Co}^{3+}-\text{Co}^{3+}$ couples are metastable and decompose into $\text{Co}^{2+}-\text{Co}^{4+}$, the disproportionation reaction is written as [6]



where the sign (\cdot) denotes the electrons situated at Co^{2+} ions and ($'$), the holes situated at Co^{4+} ones. This reaction involves only the excited cobalt ions having electrons on the e_g sublevels, that is, the ions in the HS or intermediate spin (IS) state with $t_{2g}^5e_g^1$ electron configurations and $s = 1$. In the following consideration, the state of Co^{3+} ions is indifferent. The thermal equilibrium condition in the disproportionation reaction has the form [6]

$$(\text{Co}^{2+})(\text{Co}^{4+})/(\text{Co}^{3+})^2 = \exp(-E_D/k_B T), \quad (5)$$

where the quantities in the left-hand side are mole fractions of the corresponding ions; ΔE_D is the free energy change of the spin system associated with the disproportionation reaction, that is, the reaction activation energy [9]. To obtain the relationship between the Co^{4+} concentration and the temperature variation, the mass balance equation [6]

$$\text{Co}^{\text{III}} + \text{Co}^{3+} + \text{Co}^{2+} + \text{Co}^{4+} = 1 \quad (6)$$

is to be taken into account, too.

Taking into consideration (1) and (4)–(6), we get

$$\text{Co}^{4+} = \frac{1 - [1 - \exp(-E_D/k_B T)]^{0.5}}{3 + \exp(\Delta/k_B T)}. \quad (7)$$

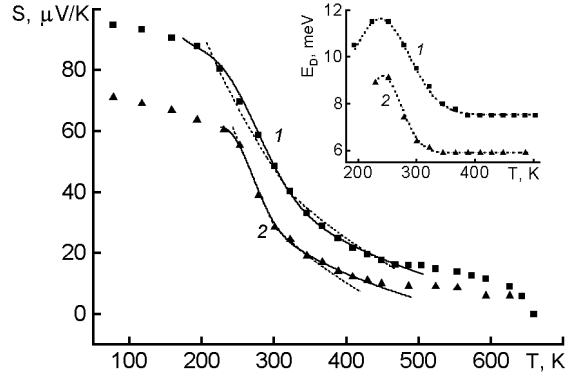


Fig. 4. Comparison of experimental $S(T)$ dependences with those calculated for $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$ (1) and $\text{Ho}_{0.35}\text{Sr}_{0.65}\text{CoO}_{3-\delta}$ (2) samples. The fitting parameter E_D as a function of temperature; the dashed lines correspond to the formula (10)

Substituting this expression into (3), the direct temperature dependence of the specific thermo-e.m.f. can be obtained. The $S(T)$ dependences calculated using (3) and (7) are close to the experimental ones in the temperature region of sharp thermo-e.m.f. dropping (Fig. 4, dashed lines). The fitting has been found to be possible only at $g_3 = 18 + 15 = 33$ corresponding to the case when the energy difference between IS and HS states of Co^{3+} ion is insignificant and $g_4 = 6$ for the HS state of Co^{4+} [16]. (The Co^{4+} ions formed under disproportionation are in the HS state). The fitting parameter E_D value in the temperature region where the thermo-e.m.f. drops sharply, as determined using the empiric formulas

$$E_D \text{ (meV)} = -0.0117 \cdot T(\text{K}) + 4.77$$

($\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$ sample)

$$E_D \text{ (meV)} = -0.03 \cdot T(\text{K}) + 10$$

($\text{Ho}_{0.35}\text{Sr}_{0.65}\text{CoO}_{3-\delta}$ sample)

decreased from 2.5 meV down to 1 meV. The disproportionation energy remained unchanged ($E_D = 1$ meV) at $T > 322$ K for $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$ and at $T > 300$ K for $\text{Ho}_{0.35}\text{Sr}_{0.65}\text{CoO}_{3-\delta}$ sample.

The spin gap width Δ is 38 meV for $\text{Ho}_{0.35}\text{Sr}_{0.65}\text{CoO}_{3-\delta}$ and 50 meV for $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$. The latter value is considerable lower than that obtained in [17] when considering the temperature dependence of electric resistance for the $\text{Ho}_{0.45}\text{Sr}_{0.55}\text{CoO}_{3-\delta}$ sample. The conductivity of that sample was described using a double-channel model. The appearance of the

Table. Dependence of Seebeck coefficient on calcium content x

x	Er _{1-x} Ca _x CoO _{3-δ}	Ho _{1-x} Ca _x CoO _{3-δ}
0.15	178	146
0.25	264	224
0.35	350	289
0.45	344	230
0.55	321	155
0.65	325	290
0.75	232	54
0.85	60	60

second channel in the semiconductor matrix was due to thermal excitations of cobalt ions from a low-spin state separated from the excited one by the energy gap $\Delta \cong 220$ meV. The difference in the spin gap values obtained using the resistive measurements and the thermoelectric ones can be explained taking into account that the relationship (1) has been written under neglect of the degeneration multiplicity g_3 of the excited Co³⁺ ions. A more precise formula for the concentration change of the excited Co³⁺ ions as a function of temperature has been obtained in [18]:

$$\frac{\text{Co}^{3+}}{\text{Co}^{\text{III}}} = \frac{g_3}{g_3 + \exp(\Delta/k_B T)}. \quad (8)$$

Taking this fact into account, the expression (7) for the temperature dependence of Co⁴⁺ ion concentration will be changed into

$$\text{Co}^{4+} = \frac{1 - [1 - \exp(-E_D/k_B T)]^{0,5}}{4 + (1/g_3)\exp(\Delta/k_B T)}. \quad (9)$$

The fitting results of S(T) dependences according to (3) and (9) are shown in Fig. 4 by solid lines. The fitting has been done at $\Delta = 240$ meV for Ho_{0.45}Sr_{0.55}CoO_{3-δ} and $\Delta = 200$ meV for Ho_{0.35}Sr_{0.65}CoO_{3-δ}. As the Sr concentration rises, the $\langle r_A \rangle$ increases, thus resulting in a decreased chemical pressure in the system and lowered effect of the crystal field. This specifies the difference in the excited spin state formation energy for the samples with different x values.

The disproportionation energy variation as a function of temperature (inset in Fig. 4) for both samples is described at a very good accuracy by the relation

$$E_D(\text{meV}) = E_{D0} + A \cdot \exp\left\{-\frac{[T(K) - T_0]^2}{B}\right\}. \quad (10)$$

The fitting parameters were as follows: $E_{D0} = 7.53$ meV, $A = 4.1$ meV, $B = 5000$ K², $T_0 = 238.4$ K for Ho_{0.45}Sr_{0.55}CoO_{3-δ} and $E_{D0} = 5.9$ meV, $A = 3.3$ meV, $B = 2000$ K², $T_0 = 242.5$ K for Ho_{0.35}Sr_{0.65}CoO_{3-δ}. The higher E_D values corresponded to the sample having a wider spin gap Δ .

The specific thermo-e.m.f. of Ca doped ceramics was considerably higher and temperature-independent (see Table). This evidences the absence of disproportionation in those samples. In fact, calcium ion radius (1 Å) is much smaller than that of strontium (1.18 Å) [3]. The level splitting energy rises due to increased overlap of cobalt 3d orbitals and oxygen p ones, so it becomes energy-unfavorable for electrons to occupy the upper σ band. That is why in the Ca-containing samples, the Co ions should be mainly in the LS state where the disproportionation is impossible. The calculation using the formula (3) has shown that in the Ca-doped samples, the g_3/g_4 ratio values are the most suitable for the case when Co³⁺ ions are in the LS state while Co⁴⁺ ones either are in the LS state, or the LS, IS, and HS state energy values for Co⁴⁺ are close to each other [16]. The high thermo-e.m.f. values are associated with low g_3/g_4 ratios for the lowered spin states. This is in agreement with the statement [18, 19] that there is no transition in the Ho_{1-x}Ca_xCoO_{3-δ} system between the LS and HS Co³⁺ states in the temperature range of 300 to 900 K.

The thermo-e.m.f. values obtained for ceramics with low Sr concentrations ($x = 0.15$; $x = 0.25$) are explainable in a similar manner.

References

1. J.Androulakis, J.Migiakis, *Appl. Phys. Lett.*, **84**, 1099 (2004).
2. J.P.Attfield, *Int. J. Inorg. Mat.*, **3**, 1147 (2001).
3. R.D.Shannon, *Acta Crystallogr.A*, **32**, 751 (1976).
4. A.A.Kozlovskii, V.P.Khirnyi, T.G.Deineka et al., *Nanosystemy, Nanomaterialy, Nanotekhnologii*, **5**, 609 (2007).
5. S.G.Ovchinnikov, Yu.S.Orlov, *Zh. Eksper. Teor. Fiz.*, **131**, 485 (2007).
6. S.R.Sehlin, H.U.Anderson, D.M.Sparlin, *Phys. Rev. B*, **52**, 11681 (1995).
7. D.M.Sparlin, R.P.Raffaella, *Ceramic Transactions, American Ceramics Society, Columbus, OH*, v.24, p.221 (1992).

8. J.P.Doumerc, *J. Solid State Chem.*, **109**, 419 (1994).
9. R.R.Heikes, R.C.Miller, R.Mazelsky, *Physika*, **30**, 1600 (1964).
10. J.W.Stevenson, M.M.Nasrallah, H.U.Anderson et al., *J.Solid State Chem.*, **102**, 175 (1993).
11. Hundley, J.J.Neumeier, *Phys.Rev.B*, **55**, 11511 (1997).
12. S.E.Dorris, T.O.Mason, *J. Am. Ceram. Soc.*, **71**, 379 (1998).
13. M.Takano, N.Nakanishi, Y.Takeda et al., *Mat. Res. Bull.*, **12**, 923 (1977).
14. M.Takano, Y.Takeda, *Bull. Inst. Chem. Res., Kyoto Univ.*, **61**, 406 (1983).
15. H.Yokokawa, N.Sakai, T.Kawada et al., *Solid State Ionics*, **52**, 43 (1992).
16. W.Koshibae, K.Tsutsui, S.Maekawa, *Phys. Rev. B*, **62**, 6869 (2000).
17. Yu.N.Tsian, V.F.Khirnyi, O.G.Shevchenko et al., *Fiz.Nizk.Temper.*, **34**, 1197 (2008).
18. Kichizo Asai, Osamu Yokokura, Nobuhiko Nishimori et al., *Phys. Rev. B.*, **50**, 3025, (1994).
19. Y.S.Im, K.H.Ryu, K.H.Kim et al., *J.Phys. Chem. Solids*, **58**, 2079 (1997).
20. I.A.Nekrasov, S.V.Streltsov, M.A.Korotin et al., arXiv:cond-mat/0306201 v1 8 Jun 2003.

Спінові стани іонів кобальту та термо-ЕРС в ербієвих та гольмієвих кобальтитах

В.П.Хірний, А.А.Козловський, О.В.Семенов, В.М.Пузіков

Досліджено температурні залежності термо-ЕРС керамік $\text{Er}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, $\text{Er}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$, $\text{Ho}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$ в області температур від 300 К (для деяких від 100 К) до 600 К. Коефіцієнт Зеебека Sr-легованих зразків знижується при зростанні вмісту стронцію та температури. Показано, що для пояснення такої поведінки необхідно враховувати розщеплення 3d-рівнів та зарядову диспропорціоналізацію іонів кобальту.