

Thermal properties of layered cobaltites $R\text{BaCo}_2\text{O}_{5.5}$ ($R = \text{Y, Gd, and Tb}$)

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Specific heat studies of a series of $R\text{BaCo}_2\text{O}_{5.5}$ ($R = \text{Y, Gd, and Tb}$) layered cobaltites are reported. They were aimed at explaining an influence of different rare-earth ions on thermal properties of these compounds and at studying phase transitions appearing in them. The studies were performed over the temperature range from 3 to 395 K, in the magnetic field ranging from 0 to 9 T. Anomalies accompanying different phase transitions were analyzed. Based on the performed supplementary Raman scattering measurements, frequencies of main optical phonon modes were determined and used for evaluation of the lattice contribution to the specific heat. Lattice, magnon, and Schottky contributions to the specific heat were separated and described theoretically. As a result, the molecular field corresponding to the R -Co exchange interactions was estimated to be ~ 1 T.

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I. INTRODUCTION

Transition-metal oxides with strongly correlated electrons, i.e., with the strong Coulomb repulsion between the outermost electrons, show numerous intriguing phenomena, like the high-temperature superconductivity or the colossal magnetoresistance. They have been attracting a great interest of researchers over the last 25 years. Within this class, the layered cobaltites $R\text{BaCo}_2\text{O}_{5.5}$, with R being a rare-earth or yttrium ion, form a distinguishing group showing a variety of intricate phenomena, related to a competition between different interactions.

For example, the competition between the crystalline electric field and the Hund coupling (i.e., the internal exchange interactions between the outer, mobile, and inner electrons of the cobalt ions) leads to the presence of the Co^{3+} ions in three different electronic configurations and spin states, i.e., in the high spin state ($t_{2g}^4 e_g^2$, $S = 2$), in the intermediate spin state ($t_{2g}^5 e_g^1$, $S = 1$), and in the low spin state ($t_{2g}^6 e_g^0$, $S = 0$). The ions in different spin states differ not only in the spin value but also in the ionic radii, which results in a strong coupling between spin, charge, orbital, and lattice degrees of freedom.¹

Moreover, the layered cobaltites show a metal-insulator transition and a large magnetoresistance, however, on the contrary to manganites, the metal-insulator transition is decoupled from the transition to a magnetically ordered phase and the magnetically ordered, low-temperature phase is the high-resistive one, whereas the paramagnetic, high-temperature phase is the low-resistive one. These two facts prove that the double exchange interaction, being the main source of the colossal magnetoresistance in manganites, is not responsible for the magnetoresistance in the layered cobaltites.

Many of the unique properties of the layered cobaltites are related to their crystalline structure, Fig. 1, which can be derived from the structure of the ideal perovskite ABO_3 in which the B positions are occupied by the cobalt ions,

whereas the A positions are occupied by the R and Ba ions in the ordered way, layer by layer, stacked along the c axis. The driving force for the ordered occupation of the A positions is a difference between the ionic radii, specifically of Ba^{2+} and R^{3+} ions.^{2,3} The oxygen content within the R -O planes can be modified over a wide range and by removing one oxygen ion from each other pair of the unit cells of the ideal perovskite one obtains the $R\text{BaCo}_2\text{O}_{5.5}$ composition, in which all cobalt ions take the $3+$ charge state. The created oxygen vacancies order at relatively high temperatures (e.g., at ~ 770 K in the case of $\text{TbBaCo}_2\text{O}_{5.5}$) and, in this way, the orthorhombic structure presented in Fig. 1, described by the $Pmmm$ space group, is formed. This kind of structure was observed in numerous $R\text{BaCo}_2\text{O}_{5.5}$ compounds,⁴ however, in dependence on the oxygen contents and on temperature, several modifications of this parent structure were found too.⁵⁻⁹ Nevertheless, all of the modifications have a general form very similar to the structure presented in Fig. 1, in which channels directed along the a axis exist. The channels facilitate diffusion of O^{2-} ions and result in a high ionic conductivity of the layered cobaltites at high temperatures. This property together with a large electronic conductivity makes these materials promising for application as cathodes for solid oxide fuel cells working at intermediate temperatures (500 – 700 °C).^{10,11}

A large magnetocrystalline anisotropy in the cobalt sublattices is a one more distinctive feature of the $R\text{BaCo}_2\text{O}_{5.5}$ compounds and allows to analyze these materials as Ising systems with the magnetic moments of cobalt ions directed along the a axis.¹²⁻¹⁴ As it was demonstrated in Ref. 15 for the case of $\text{GdBaCo}_2\text{O}_{5.5}$, the cobalt magnetic moments are strongly confined to the a direction and the magnetic field of 7 T applied along the b or c direction is not able to align the magnetic moments parallel to these directions. It causes only a partial tilting of the spins (in each sublattice) from their easy axis. Based on the magnetization data, the anisotropy energy was estimated

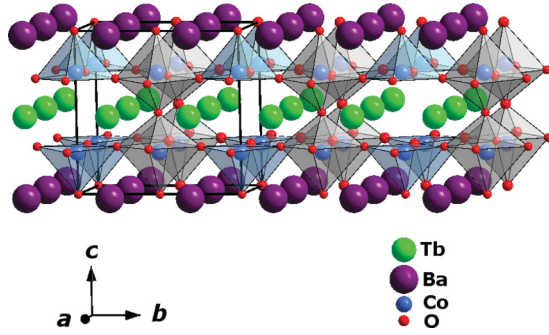


FIG. 1. (Color online) Orthorhombic $Pmmm$ structure of $RBaCo_2O_{5.5}$.

to be of the order of 10 meV/Co (by dividing this value by the Boltzmann's constant k_B , we obtain the value ~ 120 K), being ca. two times larger for the c than for the b direction.^{15,16}

The unique set of properties of the layered cobaltites results in their very rich phase diagram, extremely sensitive to the oxygen content, with numerous phase transitions of different nature, both spontaneous and induced by magnetic field.^{16–18} In the majority of the $RBaCo_2O_{5.5}$ compounds, we observe the following sequence of transformations on lowering temperature: the ordering of oxygen vacancies, the metal-insulator transition, the transition from the paramagnetic to a ferrimagnetic phase, the transition from the ferrimagnetic to an antiferromagnetic state, AF1, the transformation from the AF1 state to the low-temperature antiferromagnetic state, AF2, and an ordering of the magnetic moments of the R^{3+} ions. Despite intensive studies, it is not clear until now whether all of these transformations have all features of well defined phase transitions and what is their physical nature. In particular, the mechanism responsible for the metal-insulator phase transition, the exact magnetic structure of the AF1 and AF2 states (in Ref. 12, both of them were reported to consist of several antiferromagnetic configurations), as well as the nature of the transformation between the AF1 and AF2 states are not known satisfactorily.

Since specific heat is the quantity sensitive to all phase transitions of different nature, e.g., magnetic, structural, metal-insulator, etc., its studies can be more informative than, for example, magnetization studies of an antiferromagnetic material near the phase transitions. Thus the specific heat studies of a series of $RBaCo_2O_{5.5}$ compounds were performed. They were aimed at (i) establishing which of the transformations occurring below 400 K are well-defined phase transitions, (ii) determining the orders of the observed phase transitions, (iii) investigating the influence of different R ions on thermal properties of the layered cobaltites, (iv) separating different contributions to the specific heat, and (v) investigating the influence of magnetic field on the observed transformations.

To achieve the assumed goal, we chose the $RBaCo_2O_{5.5}$ compounds with R being (i) yttrium, which is nonmagnetic and thus makes it possible to study properties of the cobalt sublattices in $RBaCo_2O_{5.5}$ compounds, (ii) gadolinium, which remains in the orbital singlet state and hence, is insensitive to the crystalline electric field but bears a non-zero spin magnetic moment ($S = 7/2$), (iii) terbium, which is both magnetic and influenced by the crystalline electric field.

II. EXPERIMENT

For performing the specific heat studies, powder samples of $YBaCo_2O_{5.49}$ (as it was reported in Ref. 16, growing a single crystal of this composition is “virtually impossible”), $GdBaCo_2O_{5.5}$, and $TbBaCo_2O_{5.51}$, prepared by a solid state reaction method (details of the preparation procedure are given in Ref. 2), and a $TbBaCo_2O_{5.5}$ single crystal grown by applying the traveling floating zone method were chosen. Oxygen content was determined by thermogravimetric analysis (hydrogen reduction) and by standard iodometric titration.

For all the samples, the specific heat was measured by means of the relaxation method, using the Physical Property Measurement System (PPMS), made by Quantum Design. In order to perform measurements of the powder samples (a review of different methods proposed for powder samples is given in Ref. 19), we used aluminum crucibles devoted to thermogravimetric analysis, commercially available from Mettler Toledo. The crucibles had a form of ~ 1.6 mm high cylinders of the diameter 6 mm, equipped with lids. The estimated uncertainty of the sample specific heat values determined in this way was $\sim 2\%$. Measurements were performed over the temperature range from 2 or 3 K (the lowest temperature was determined by the mass of the particular sample and the thermal coupling to the calorimeter attained for it) to 385 K, for zero magnetic field and for several fixed magnetic field values ranging from 1 up to 9 T. The specific heat was measured every 0.2 K in the low-temperature range, i.e., below 15 K, every 0.25 K in regions, in which appearance of phase transitions was expected, e.g., between 220 and 360 K for $TbBaCo_2O_{5.5}$, and not more sparsely than every 5 K in remaining ranges. In all figures presented below, not all experimental points are marked with symbols to maintain legibility.

In order to determine energies of main optical phonon modes, needed for evaluating the lattice contribution to the specific heat, supplementary Raman scattering studies have been performed for $RBaCo_2O_{5.5}$ compounds with R being Tb, Gd, and Eu. The Raman scattering measurements were performed in quasi-backscattering geometry with the excitation line $\lambda = 514.5$ nm of an Ar laser. The laser power of 10 mW was focused to a 0.1 mm diameter spot on the sample surface. Spectra of the scattered radiation were collected by a DILOR-XY triple spectrometer and recorded by a nitrogen cooled charge-coupled device detector with a spectral resolution of < 0.5 cm^{-1} . Temperature dependences were measured in a continuous helium flow cryostat from 5 K to room temperature. Experiments at elevated temperatures up to 390 K were carried out using a helium gas filled heating stage. Measurements were performed in different polarization configurations with the laboratory axes x , y , and z being parallel to the crystallographic axes a , b , and c .

III. RESULTS AND ANALYSIS

A. Specific heat studies

Results of the specific heat measurements performed are presented in Fig. 2. They show that the temperature dependences of specific heat are qualitatively very similar for all the studied compounds and differ only in temperatures at which anomalies accompanying particular phase transitions appear.

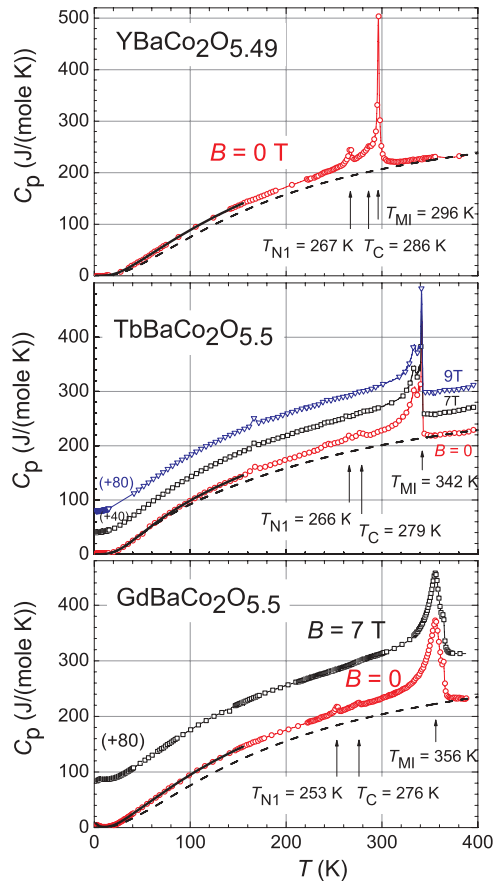


FIG. 2. (Color online) Temperature dependences of specific heat measured for $R\text{BaCo}_2\text{O}_{5.5}$ compounds ($R = \text{Y, Gd, and Tb}$) in zero magnetic field and for several fixed magnetic field B values (for the $\text{TbBaCo}_2\text{O}_{5.5}$ single crystal, B was applied along the c axis). Curves measured at different B are shifted along the C_p axis by the values given in parentheses. The determined phonon contributions C_{ph} are plotted with dashed lines. Thick solid lines extending from 2 K to ~ 160 K present the sum of the phonon C_{ph} , nuclear C_{n} , and magnon C_{ma} contributions for the yttrium and terbium compounds, and the sum of C_{ph} , C_{n} , C_{ma} , and the Schottky C_{Sch} contributions for the gadolinium compound. The panels are placed in the order of increasing R ion radius from top to bottom.

In Fig. 3, the temperatures at which the phase transitions were observed in the present studies, are put together with the literature data and presented as a function of the effective ionic radius of the R^{3+} ion (the radii were taken from Ref. 23, for the coordination number equal to nine, i.e., for the number closest to the case of the layered cobaltites). The specific heat anomalies become better visible after extracting the lattice contribution to the specific heat, as it is shown in Fig. 4. Details of the method used for estimation of the lattice contribution will be presented in the next section.

In general, for all the compounds studied, the metal-insulator transition, occurring at the T_{MI} temperature, was accompanied by a symmetric, very sharp and high anomaly. This strongly suggested that this was the first-order transition, though the thermal hysteresis, which is the most characteristic feature of first-order transitions,^{24,25} was not observed in the present studies (i.e., the anomaly appeared at the same temperature independently whether the measurements were

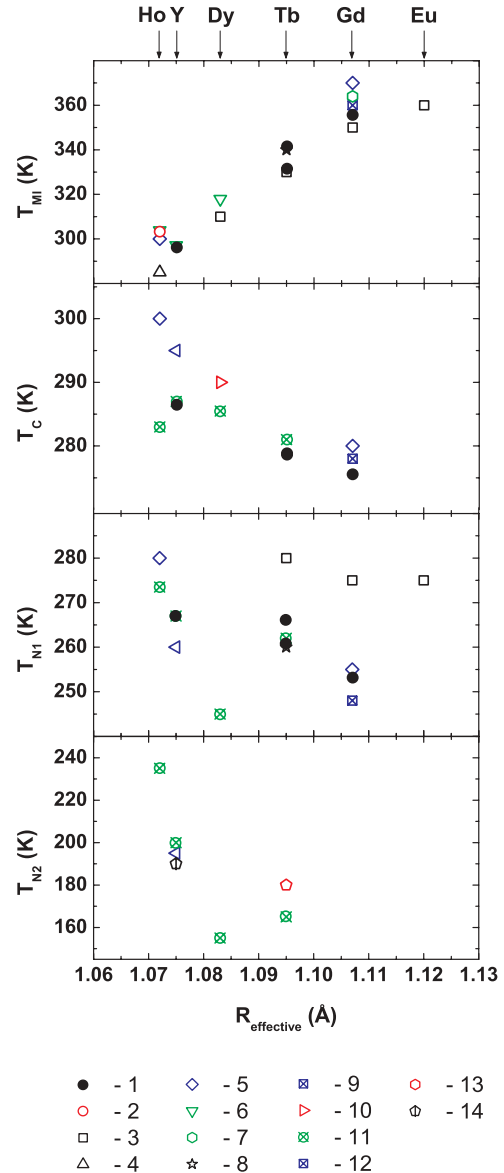


FIG. 3. (Color online) Dependences of the metal-insulator transition temperature T_{MI} , of the Curie temperature T_{C} , of the temperature of the phase transition from the ferrimagnetic to the antiferromagnetic AF1 state, T_{N1} , and of the temperature of transformation between AF1 and AF2 antiferromagnetic states on the effective radius of R^{3+} ions in the $R\text{BaCo}_2\text{O}_{5.5}$ compounds. The numbers indicate the following sources of the presented data: data 1 are the results of the present studies, data 2 are from Ref. 20, 3 are from Ref. 4, 4 are from Ref. 21, 5 are from Ref. 1, 6 are from Ref. 17, 7 are from Ref. 16, 8 are from Ref. 2, 9 are from Ref. 3, 10 are from Ref. 22, 11 are from Ref. 12, 12 are from Ref. 5, 13 are from Ref. 7, and 14 are from Ref. 31.

performed on heating or on cooling the sample). However, taking into account that the presence of a hysteresis is the sufficient condition only but not the necessary condition, the interpretation of the metal-insulator phase transition as the first-order one seems to be well based. For the case of $\text{TbBaCo}_2\text{O}_{5.5}$ single crystal, this anomaly is split into three ones. We attribute this to the fact that in the traveling floating zone method, used for growing the single crystal, gradients of the oxygen content are introduced inherently. In

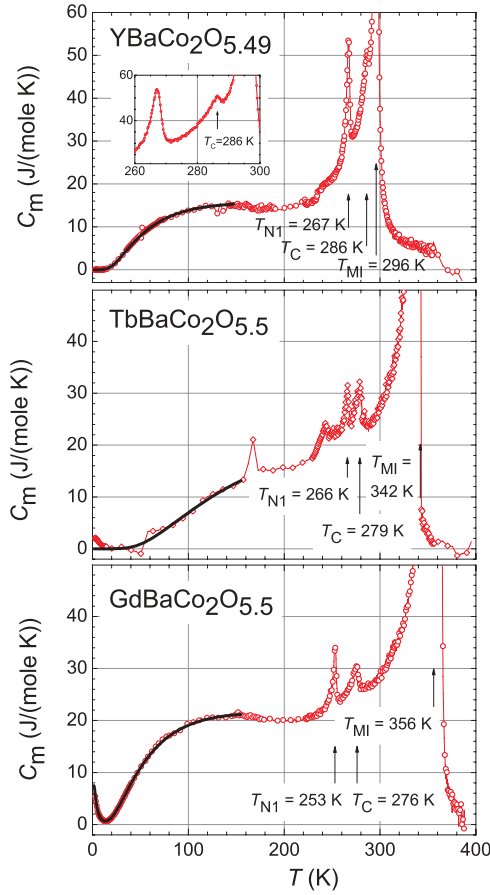


FIG. 4. (Color online) Temperature dependences of the magnetic contribution, C_m , to the specific heat measured for $R\text{BaCo}_2\text{O}_{5.5}$ compounds ($R = \text{Y, Gd, and Tb}$) in zero magnetic field. C_m was determined by subtracting the determined phonon contribution C_{ph} from the measured specific heat C_p . Thick solid lines extending from 2 K to ~ 160 K present the sum of the nuclear C_n and magnon contributions C_{ma} for the yttrium and terbium compounds, and the sum of C_n , C_{ma} , and the Schottky C_{Sch} contributions for the gadolinium compound. Anomalies accompanying various phase transitions are indicated by arrows.

the case of layered cobaltites in which the temperature of the metal-insulator phase transition is extremely sensitive to the oxygen content,^{16–18} this leads to splitting of the specific heat anomaly. To verify this explanation, we performed specific heat measurements of the powder $\text{TbBaCo}_2\text{O}_{5.51}$ sample and we found for it no splitting of the anomaly at T_{MI} . As illustrates Fig. 3, the temperature of the metal-insulator transition increases nearly linearly with the increase of the effective radius of the R ion.

The phase transition from the paramagnetic to the ferrimagnetic phase, occurring at the temperature T_C , distinctly lower than T_{MI} , is accompanied by a weak, λ -shaped anomaly. Under influence of the magnetic field, this anomaly smears and shifts towards higher temperatures, i.e., it presents the behavior typical of anomalies accompanying second-order transitions from a paramagnetic phase to a ferromagnetic or a ferrimagnetic one. As it follows from Fig. 3, the T_C temperature decreases with the increase of the radius of the R ion.

The phase transition from the ferrimagnetic phase to the antiferromagnetic state AF1 (being a mixture of several antiferromagnetic configurations¹²) is accompanied by a symmetric anomaly suggesting the first-order character of this transformation. As illustrates Fig. 3, it is difficult to notice any rule in dependence of the temperature of this transition on the R ion radius. Tentatively, this can be attributed to the fact that various antiferromagnetic configurations, of which the AF1 state is composed,¹² differ in energy slightly. Thus, the exact phase composition of the AF1 state and the temperature, at which the transition to this state appears, strongly depend on the oxygen stoichiometry and it is difficult to find a rule from the comparison of the samples that were obtained in different technological processes and differ slightly in the oxygen content.

No specific heat anomalies were found at the transformation point between AF1 and AF2 states in yttrium and gadolinium compounds, so, in our opinion, this transformation should not be considered as a well defined phase transition. In fact, a small maximum observed for the terbium cobaltite at 167 K coincides with the temperature of the AF1-AF2 transformation reported in Ref. 12 (in Ref. 7, a higher temperature of 180 K is reported as the point of this transition) and it becomes even more pronounced with increase of the external magnetic field, however, it was unreproducible and could not be reproduced in measurements performed with a smaller temperature step. Thus it can not be interpreted as the indication of the well defined phase transition.

As Fig. 5 illustrates, the most distinct qualitative difference between the temperature dependences of specific heat of the $\text{YBaCo}_2\text{O}_{5.49}$ compound and of the compounds containing magnetic R^{3+} ions occurs below 10 K, where an upturn of the specific heat on lowering temperature is observed for the compounds containing magnetic R^{3+} ions. Figures 6 and 7 show that this is related to a wide maximum, shifting towards higher temperatures under influence of the magnetic field. This maximum has no features of a λ -shaped anomaly, which could testify to the presence of a phase transition consisting in ordering of magnetic moments of the R^{3+} ions. Thus we interpret it as a Schottky anomaly related to excitations of the R ions to higher energy states of their ground multiplet, split by a crystalline electric field, CEF, and the R -Co and R - R exchange interactions. As it will be shown in the next section, calculations performed for the $\text{GdBaCo}_2\text{O}_{5.5}$ compound confirmed this interpretation. (The first trial of analysis of our preliminary measurements of the Schottky anomaly in the terbium compound was proposed in Ref. 32. However, as the next detailed measurements showed, the dependences for zero magnetic field and for the field of 5 T as well as the interpretation assigning a substantial role in appearance of the Schottky anomaly to nuclear magnetic moments, presented in Ref. 32, were incorrect.)

B. Decomposition of the specific heat into various contributions

The total specific heat of the $R\text{BaCo}_2\text{O}_{5.5}$ compounds can be presented as a sum of two main contributions:

$$C_p(T, B) = C_{\text{ph}}(T) + C_m(T, B). \quad (1)$$

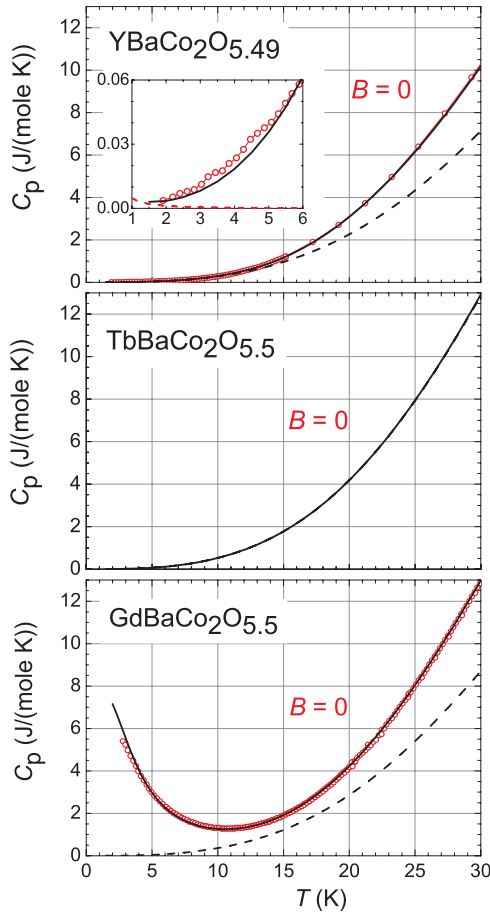


FIG. 5. (Color online) Low-temperature parts of the temperature dependences of specific heat measured for $R\text{BaCo}_2\text{O}_{5.5}$ compounds ($R = \text{Y, Gd, and Tb}$) in zero magnetic field. The determined phonon contributions C_{ph} are plotted with dashed lines. Thick solid lines present the sum of the determined phonon C_{ph} , nuclear C_{n} , and magnon C_{ma} contributions for the yttrium and terbium compounds, and the sum of the determined C_{ph} , C_{n} , C_{ma} , and Schottky C_{Sch} contributions for the gadolinium compound. In the inset to the panel of the yttrium compound, the dependence measured up to 6 K is presented in the enlarged scale, the calculated nuclear contribution $C_{\text{n}}(T)$ is plotted with the dashed (red) line, and the sum of the C_{ph} , C_{n} , and C_{ma} contributions is plotted with the solid (black) line.

In this equation, C_{ph} denotes a lattice (phonon) contribution, depending on temperature and independent of an external magnetic field, and C_{m} denotes a magnetic contribution depending on both temperature and magnetic field. The magnetic contribution, in turn, can be decomposed into (i) a nuclear specific heat C_{n} , coming from excitations of those ionic nuclei that possess nonzero nuclear magnetic moments and are subjected to an influence of a nonzero hyperfine field, (ii) the Schottky contribution C_{Sch} , coming from excitations of R ions to different energy levels split by a crystalline electric field, exchange interactions, and an external magnetic field, (iii) a magnon contribution C_{ma} , coming from magnon excitations of the cobalt sublattices below T_{C} that can be described in models of non-interacting magnons, based on the Holstein-Primakoff²⁶ approach, and (iv) a remaining contribution C_{rem} , related to excitation of interacting magnons (high-temperature

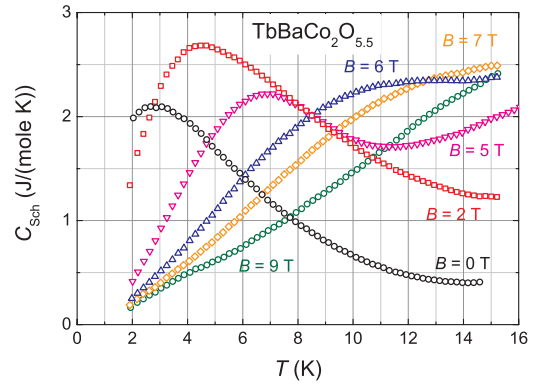


FIG. 6. (Color online) Schottky contribution C_{Sch} to the specific heat of $\text{TbBaCo}_2\text{O}_{5.5}$ determined by subtracting the sum of phonon C_{ph} , nuclear C_{n} , and magnon C_{ma} contributions, determined for the case of zero magnetic field, from the measured specific heat C_{p} . Under influence of the magnetic field the Schottky anomaly shifts towards higher temperatures and smears.

region in which Holstein-Primakoff approximation breaks) and to phase transitions, e.g., a latent heat connected with first-order transitions or fluctuations occurring in the vicinity of second-order transitions. Thus the magnetic specific heat can be presented in the form:

$$C_{\text{m}} = C_{\text{n}} + C_{\text{Sch}} + C_{\text{ma}} + C_{\text{rem}}. \quad (2)$$

Since for the $R\text{BaCo}_2\text{O}_{5.5}$ layered cobaltites the contributions enumerated above dominate in different temperature ranges, it was possible to separate them. Before presenting the separation procedure that was used, we will describe particular contributions in greater detail.

1. Lattice contribution to the specific heat C_{ph}

To determine the phonon specific heat, which is the main contribution that must be extracted to perform more detailed analysis of the magnetic contributions, we used the following approach. We assumed that the $R\text{BaCo}_2\text{O}_{5.5}$ unit

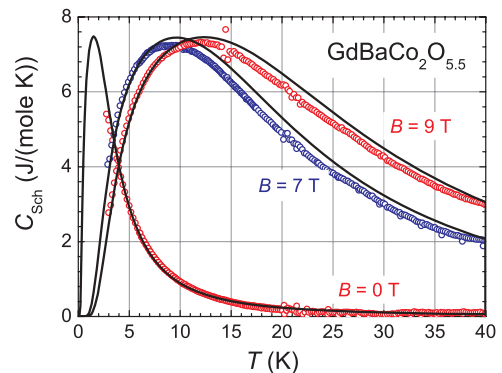


FIG. 7. (Color online) Schottky contribution C_{Sch} to the specific heat of $\text{GdBaCo}_2\text{O}_{5.5}$ determined by subtracting the sum of phonon C_{ph} , nuclear C_{n} , and magnon C_{ma} contributions, determined for the case of zero magnetic field, from the measured specific heat C_{p} . Under influence of the magnetic field the Schottky anomaly shifts towards higher temperatures and smears. Thick solid lines present dependences calculated for $B_{\text{ex}} = 1.10$ T according to Eq. (6) for the case $B = 0$ and according to Eq. (7) for $B \neq 0$.

cell (see Fig. 1) contains the following two chemical formulas: $R\text{BaCo}_2\text{O}_6$ and $R\text{BaCo}_2\text{O}_5$. Thus, the atoms contained in a one crystal unit cell have $3(10 + 9) = 57$ degrees of freedom and we can expect the presence of 57 phonon branches for this crystal, three of which are acoustic and the remaining 54 are optical ones. Then, the Debye model seems to be the best for describing the acoustic modes, whereas the Einstein model seems to be better for describing the optical modes. However, there is no certainty that all optical modes are dispersionless (as the Einstein model assumes), so it is possible that also some of them will be described better within the Debye model. Thus, to calculate the heat capacity of a one mole of the $R\text{BaCo}_2\text{O}_{5.5}$ chemical compound, we must calculate the heat capacity of $N_A/2$ crystal unit cells (N_A denotes the Avogadro's constant). It can be done according to the formula

$$C_{\text{ph}}(T) = \frac{1}{(1-\alpha T)} \frac{k_B N_A}{2} \left[3n_D \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx + \sum_{i=1}^{n_O} n_i \left(\frac{\theta_i}{T} \right)^2 \frac{e^{\frac{\theta_i}{T}}}{(e^{\frac{\theta_i}{T}} - 1)^2} \right], \quad (3)$$

where k_B , θ_D , n_D , n_O , θ_i , n_i , denote, respectively, the Boltzmann's constant, the Debye temperature, the number of modes considered within the Debye model (as explained above, this number should not be smaller than three), the number of nondispersive optical branches treated within the Einstein model, energy of particular Einstein's branches (expressed in temperature units), the number of optical modes assigned to the i th branch. Additionally, the condition $n_D + \sum_{i=1}^{n_O} n_i = 57$ should be fulfilled. Since both the Debye and the Einstein model were elaborated for the systems of constant volume, whereas the measurements were performed at constant pressure, it was necessary to take into account the increase of the phonon specific heat related to the thermal expansion of the crystal lattice. It has been done by introducing the coefficient $1/(1-\alpha)$ into Eq. (3), i.e., by using the method proposed in Ref. 27. (In fact, the method proposed in Ref. 27 allows to introduce various α coefficients for each phonon mode, however, to avoid introducing too many fitted parameters, we simplified the description by introducing only one coefficient α , common for all modes.) It should be stressed that to determine the lattice specific heat for the wide temperature range, for which our measurements were performed, i.e., from 3 to nearly 400 K, it was necessary to use in Eq. (3) the Debye integral, not the low-temperature approximation, in which one assumes that the lattice specific heat is proportional to T^3 .

In order to make use of Eq. (3), it is necessary to know the energies of optical phonons. Thus, we performed supplementary studies of Raman scattering for a series of $R\text{BaCo}_2\text{O}_{5.5}$ compounds. Their results, presented in Fig. 8, show that four main optical phonons of energy 247 cm^{-1} ($\approx 355 \text{ K}$), 300 cm^{-1} ($\approx 432 \text{ K}$), 444 cm^{-1} ($\approx 639 \text{ K}$), and 610 cm^{-1} ($\approx 878 \text{ K}$) appear in all the compounds studied (in parentheses, there are given the energies of optical phonons expressed in temperature units). Then, we assumed, that the lattice specific heat of all the $R\text{BaCo}_2\text{O}_{5.5}$ compounds studied can be described adequately, if the four dispersionless Einstein branches of optical phonons of the energies given above will be considered (i.e., if we take $n_O = 4$) and the numbers

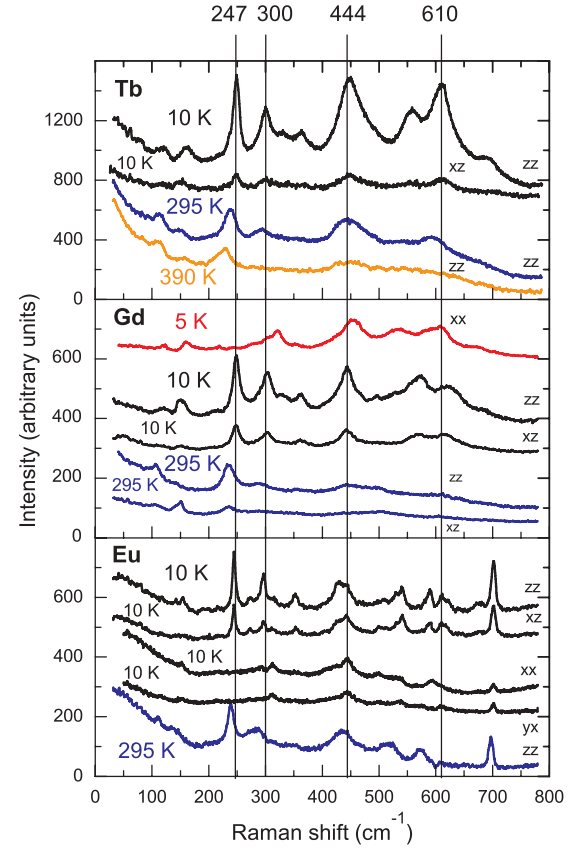


FIG. 8. (Color online) Selected temperature-dependent Raman spectra of $R\text{BaCo}_2\text{O}_{5.5}$ ($R = \text{Tb, Gd, and Eu}$) compounds measured in different scattering configurations.

determining distribution of all phonon modes into the acoustic Debye modes and the four optical Einstein modes, i.e., the numbers n_D and n_i , will be treated as fitted parameters. (C_{ph} determined in this way for the studied compounds is plotted in Figs. 2 and 5 with thick dashed lines.)

2. Nuclear contribution to the specific heat C_n

Since cobalt nuclei possess a nonzero nuclear spin $I = 7/2$ and a related to it nonzero magnetic moment of $4.627\mu_N = g_N I$, where $g_N \approx 1.32$ and μ_N denotes the nuclear magneton, excitations between their magnetic levels, split under influence of a hyperfine field, can be a main source of the nuclear contribution to the specific heat. However, as it was shown in Ref. 28, based on NMR studies of the $\text{YBaCo}_2\text{O}_{5.5}$ compound, the hyperfine field B_{hyp} acting on Co ions located in different positions is different. The largest $B_{\text{hyp}} \approx 21.6 \text{ T}$ acts on the cobalt nuclei located in the pyramidal surroundings. The hyperfine field acting on the cobalt nuclei in octahedral sites is, at least, one order of magnitude smaller, hence their contribution to specific heat above 2 K is negligible. Thus the nuclear contribution to the molar specific heat was estimated (without fitting) according to the formula

$$C_n(T) = \frac{N_A (g_N \mu_N B_{\text{hyp}})^2 I(I+1)}{3k_B} \frac{1}{T^2} = \frac{a_{-2}}{T^2}, \quad (4)$$

and it was assumed to be the same for all $R\text{BaCo}_2\text{O}_{5.5}$ compounds. The estimated value of the a_{-2} parameter is

TABLE I. Determined parameters describing phonon C_{ph} , nuclear C_{n} , magnon C_{ma} , and Schottky C_{Sch} contributions to the specific heat of the $R\text{BaCo}_2\text{O}_{5.5}$ compounds ($R = \text{Y, Gd, and Tb}$). For each parameter, an estimated uncertainty of the last digit is given in parentheses, e.g., 1.10(5) means 1.10 ± 0.05 .

R	Y	Tb	Gd
a_{-2} (JK/mole)	$\approx 4.7610^{-3}$	$\approx 4.7610^{-3}$	$\approx 4.7610^{-3}$
a_1 [J/(mole K ^{1/2})]	343(3)	775(10)	474(5)
a_2 (K)	91(1)	241(2)	91(2)
α (1/K)	0.00035(5)	0.00028(1)	0.00034(1)
n_{D}	13(1)	21(1)	13(1)
θ_{D} (K)	246(3)	235(3)	227(1)
n_1 ($\theta_1 = 355$ K)	13(1)	11(1)	7(1)
n_2 ($\theta_2 = 432$ K)	6(1)	3(1)	17(1)
n_3 ($\theta_3 = 639$ K)	14(1)	2(1)	3(1)
n_4 ($\theta_4 = 878$ K)	11(1)	20(1)	17(1)
B_{ex} (T)			1.10(5)

given in Table I. It should be stressed that the nuclear contribution decreases rapidly with increasing temperature, whereas the other contributions increase. Thus it soon becomes negligible. This contribution is the most important for the case of the yttrium compound, for which no upturn appears at low temperatures. For this compound, C_{n} constitutes ca. 32% of the measured specific heat at 2 K but it decreases to a negligible value of 0.2 % at 6 K. For the terbium/gadolinium compound, C_{n} decreases from 0.03/0.01 % of the total specific heat value at 3 K to the negligible value of 0.01/0.006 % at 6 K.

3. Schottky contribution to the specific heat C_{Sch}

If we deal with an object that has n discrete energy states, a contribution to the specific heat originating from thermal excitation of this object to its n energy levels is called the Schottky anomaly. In a general case, the Schottky anomaly is given by the expression

$$C_{\text{Sch}}(T) = \frac{k_{\text{B}} N_{\text{A}}}{T^2} \left[\frac{\sum_{i=1}^n E_i^2 e^{-\frac{E_i}{T}}}{\sum_{i=1}^n e^{-\frac{E_i}{T}}} - \left(\frac{\sum_{i=1}^n E_i e^{-\frac{E_i}{T}}}{\sum_{i=1}^n e^{-\frac{E_i}{T}}} \right)^2 \right]. \quad (5)$$

In the $R\text{BaCo}_2\text{O}_{5.5}$ cobaltites, magnetic R ions for which the ground multiplet can be split by a crystalline electric field and by exchange R -Co and R - R interactions, can be a source of the Schottky anomaly. While for the yttrium compound this anomaly is absent (Y^{3+} is a nonmagnetic ion) and for the terbium compound, it is very difficult to determine this anomaly analytically, because the energy level scheme of a Tb^{3+} ion in this compound (occurring as the result of a joint action of the crystal field and the exchange interactions) is not known, for the gadolinium compound Eq. (5) can be expressed analytically. If we take into account that the Gd^{3+} ion is insensitive to the crystal field (for its ground multiplet, the orbital angular momentum is equal to zero) and analyze the exchange interactions within the molecular field approximation, then in zero external magnetic field, the energy levels will split under influence of the molecular field B_{ex} only

and the Eq. (5) will take a form

$$C_{\text{Sch}}(T, B_{\text{ex}}) = \frac{N_{\text{A}}(g\mu_{\text{B}}B_{\text{ex}})^2}{4k_{\text{B}}T^2} \left\{ 4S(S+1) - (2S+1)^2 \times \coth^2 \left[\frac{g\mu_{\text{B}}(2S+1)B_{\text{ex}}}{2k_{\text{B}}T} \right] + \coth^2 \left(\frac{g\mu_{\text{B}}B_{\text{ex}}}{2k_{\text{B}}T} \right) \right\}, \quad (6)$$

where S and g denote, respectively, the spin and the g factor of the magnetic ion (for Gd ion, $g = 2$). Then, B_{ex} remains the only fitted parameter. Equation (6) becomes more complex for a nonzero external magnetic field, B . If we consider a powder sample of $\text{GdBaCo}_2\text{O}_{5.5}$, in which all powder particles are fixed and can not move in the field (i.e., the sample that was used in our studies), then B_{ex} is differently oriented inside each single crystalline particle, because its orientation is determined by the orientation of the crystallographic axes. Then, in the powder sample, there are equally probable all possible mutual orientations of B_{ex} and B . Thus, for the case of $B > B_{\text{ex}}$, after performing the averaging over all allowed mutual orientations of B and B_{ex} (when performing averaging, we considered the mathematically equivalent case, in which the direction of the exchange field is fixed and all orientations of the external field are allowed and equally probable), we obtain the following formula:

$$C_{\text{Sch-av}}(T, B, B_{\text{ex}}) = \frac{N_{\text{A}}(g\mu_{\text{B}})^2}{4k_{\text{B}}T^2} \left\{ 4S(S+1)(B_{\text{ex}}^2 + B^2) - \frac{8(k_{\text{B}}T)^4}{B(g\mu_{\text{B}})^4 B_{\text{ex}}} \times \left[\frac{1}{(2S+1)^2} \int_{y_3}^{y_4} y^3 \coth^2(y) dy - \int_{y_1}^{y_2} y^3 \coth^2(y) dy \right] \right\}, \quad (7)$$

where

$$y_1 = \frac{g\mu_{\text{B}}(B - B_{\text{ex}})}{2k_{\text{B}}T}, \quad y_2 = \frac{g\mu_{\text{B}}(B + B_{\text{ex}})}{2k_{\text{B}}T}$$

$$y_3 = (2S+1)y_1, \quad y_4 = (2S+1)y_2.$$

[The Schottky contribution determined for the gadolinium compound by using Eqs. (6) and (7) is plotted in Fig. 7 with the thick solid line].

4. Magnon contribution to the specific heat C_{ma}

As it was mentioned above, the $R\text{BaCo}_2\text{O}_{5.5}$ cobaltites show a very large magnetic anisotropy and behave like Ising systems. Thus, in order to describe the contribution related to excitation of magnons in the antiferromagnetically ordered cobalt sublattices to the specific heat, we applied the model proposed in Ref. 29 in which magnons in highly anisotropic materials and their contribution to specific heat were considered within the Holstein-Primakoff²⁶ approximation of noninteracting magnons. This model was successfully applied for analysis of the magnon specific heat in other anisotropic quasi-two-dimensional materials.³⁰ According to it, C_{ma} is described by the formula

$$C_{\text{ma}} = \frac{a_1}{\sqrt{T}} \exp\left(-\frac{a_2}{T}\right) \text{ for } \mu_{\text{B}}B_{\text{a}} > \mu_{\text{B}}B > Tk_{\text{B}}, \quad (8)$$

where a_1 and a_2 are fitted parameters, B denotes an external magnetic field, and B_a a parameter of the order of anisotropy and exchange fields. Since it is usually assumed that models of noninteracting magnons are applicable up to temperatures of the order of $1/2$ of the ordering temperature (for the compounds studied $T_{N1} \sim 260$ K) and the anisotropy energy (and also the $\mu_B B_a$ value) for the $R\text{BaCo}_2\text{O}_6$ compounds is ~ 120 K, we assumed that this model should be adequate for the temperature range from the lowest temperatures up to $T \sim 120$ K. [The magnon contribution determined for the yttrium and terbium compounds by using Eq. (8) is plotted in Fig. 4 with the thick solid lines].

5. Decomposition procedure

Due to different properties of the R ions contained in the studied compounds, decomposition of the measured specific heat into various contributions had to be performed in different ways. It was assumed that particular contributions are given by Eqs. (3), (4), (6), and (8) and that for sufficiently high temperatures, i.e., above T_{MI} , C_{ph} is the only contribution to the specific heat. Then, to analyze the dependences measured in zero magnetic field, (i) for $\text{YBaCo}_2\text{O}_{5.49}$, it was assumed that $C_p(T) = C_{ph}(T) + C_n(T) + C_{ma}(T)$ for the temperatures $2 \text{ K} < T < 150 \text{ K}$ and $C_p(T) = C_{ph}(T)$ for $T > 365 \text{ K}$. Next, these dependences were fitted to the experimental points measured within the indicated temperature ranges, by treating a_1 , a_2 , α , n_D , θ_D , and n_i for $i = 1, 2$, and 3 as fitted parameters. (For all the compounds, n_4 was not fitted but determined from the condition $n_4 = 57 - n_D - \sum_{i=1}^3 n_i$.)

(ii) For $\text{TbBaCo}_2\text{O}_{5.5}$, it was assumed that $C_p(T) = C_{ph}(T) + C_n(T) + C_{ma}(T)$ for the temperatures $13 \text{ K} < T < 155 \text{ K}$ and $C_p(T) = C_{ph}(T)$ for $T > 365 \text{ K}$. This choice of the low-temperature limit followed from the fact that below 13 K the Schottky contribution is not negligible and there is no analytical description for it for the terbium compound. These dependences were fitted to the experimental points measured within the indicated temperature ranges, by treating a_1 , a_2 , α , n_D , θ_D , and n_i for $i = 1, 2$, and 3 as fitting parameters.

(iii) For $\text{GdBaCo}_2\text{O}_{5.5}$ it was assumed that $C_p(T) = C_{ph}(T) + C_n(T) + C_{Sch} + C_{ma}(T)$ for the temperatures $2.8 \text{ K} < T < 155 \text{ K}$ and $C_p(T) = C_{ph}(T)$ for $T > 380 \text{ K}$. By using the fact that the Schottky anomaly is described by Eq. (6) for this compound, these dependences were fitted to the experimental points measured within the indicated temperature ranges, by treating B_{ex} , a_1 , a_2 , α , n_D , θ_D , and n_i for $i = 1, 2$, and 3 as fitting parameters.

All the parameters describing the specific heat of the compounds studied, i.e., those that were calculated based on the literature data (a_{-2}), those that were determined experimentally (θ_i) and those that were determined as the result of fitting, are collected in Table I. An uncertainty of the particular parameters was estimated by keeping all other parameters fixed and checking that no noticeable change of the theoretical curve appears for the values of the examined parameter lying within the uncertainty range, whereas for the values beyond that range, fit quality deteriorates evidently. The lattice contribution, which is the largest one, determined for all studied compounds has been plotted in Figs. 2 and 5 with thick dashed line. Having it determined, we could

extract it from the measured specific heat and, as it was mentioned above, make other contributions, in particular the anomalies accompanying the phase transitions, better visible. The differences between the measured specific heat and the determined dependences $C_{ph}(T)$ are presented in Fig. 4. In this figure, there are also plotted (with the thick solid lines) the determined magnon contributions for the cases of the yttrium and terbium compounds, and the sum of the magnon and Schottky contributions for the gadolinium compound. As it follows from the figure, the chosen model of magnons in anisotropic antiferromagnets²⁹ describes satisfactorily the magnon contribution to the specific heat of the $R\text{BaCo}_2\text{O}_{5.5}$ cobaltites within the expected temperature range, which confirms the presence of a large magnetocrystalline anisotropy in the cobalt sublattices.

The Schottky contributions, extracted by subtracting the sum of C_n , C_{ph} , and C_{ma} from the specific heat measured for the terbium and gadolinium compounds, are presented in Figs. 6 and 7. The Schottky contributions for the dependences measured in a nonzero external magnetic field were extracted by using the approximation that neither C_n nor C_{ma} depends on the external field B . This approximation seems to be acceptable, because in the temperature range, where the Schottky anomaly appears, C_n and C_{ma} are substantially smaller than the Schottky contribution. Moreover, the model presented in Ref. 29 considers only the behavior of the magnon contribution for the field directed along the easy direction and perpendicular to it, whereas for the case of the $\text{GdBaCo}_2\text{O}_{5.5}$ powder sample it would be necessary to now this contribution for an arbitrary orientation of the field. For both terbium and gadolinium compounds, under influence of the magnetic field, the wide low-temperature maximum shifts towards higher temperatures and smears. Figure 7 proves that the dependence given by Eq. (6) (which should be adequate for the gadolinium compound) in which the B_{ex} parameter takes the value $(1.10 \pm 0.05) \text{ T}$, reproduces satisfactorily the low-temperature maximum (this dependence is plotted with the thick solid line). It was checked that the deviations of B_{ex} by $\pm 0.05 \text{ T}$ from the value 1.10 cause a noticeable deterioration of the fit quality. Moreover, the dependences given by Eq. (7) plotted for $B_{ex} = 1.10 \text{ T}$ and $B = 7$ and 9 T satisfactorily reproduce the low temperature maxima extracted from the dependences measured in the field of 7 and 9 T . We attribute a certain discrepancy observed for $T > 15 \text{ K}$ to not taking into account the influence of B on the magnon specific heat. Thus, we conclude that the parameter $B_{ex} = (1.10 \pm 0.05) \text{ T}$ represents the real strength of the R -Co exchange interactions in the $R\text{BaCo}_2\text{O}_{5.5}$ compounds and that the good description of the low temperature maxima by Eqs. (6) and (7) proves that their interpretation as the Schottky anomalies, not as the λ anomalies related to the appearance of a spontaneous long range ordering within the R sublattice, is correct.

Additionally, based on the dependences presented in Figs. 6 and 7, the magnetic entropies related to the Schottky anomalies per one R ion were calculated by using the formula: $S_{Sch}(T, B) = \int_0^T [C_{Sch}(T', B)/T'] dT' / (N_A k_B)$. It was found that for the gadolinium compound $S_{Sch}(15 \text{ K}, 0 \text{ T}) = 2.06 \approx \ln(8)$ (which means that all levels of the $J = 7/2$ ground multiplet of the Gd^{3+} ion are populated at 15 K in zero magnetic field) and $S_{Sch}(15 \text{ K}, 9 \text{ T}) = 1.23 \approx \ln(3.4)$. For the

terbium compound it was found that $S_{\text{Sch}}(15 \text{ K}, 0 \text{ T}) = 0.56 \approx \ln(1.8)$ and $S_{\text{Sch}}(15 \text{ K}, 9 \text{ T}) = 0.23 \approx \ln(1.3)$, which means that in the field up to 9 T, only two levels of the $J = 6$ ground multiplet of the Tb^{3+} ion contribute to the Schottky anomaly.

IV. CONCLUSIONS

The specific heat studies of the $R\text{BaCo}_2\text{O}_{5.5}$ ($R = \text{Y}$, Gd , and Tb) layered cobaltites showed that the following transformations are well defined phase transitions: from the metallic to the insulating state (the first-order transition), from the paramagnetic to the ferrimagnetic state (the second-order transition), and from the ferrimagnetic to the antiferromagnetic AF1 state (the first-order transition). The transformation between AF1 and AF2 states is not accompanied by a specific heat anomaly, which would allow to call this transformation a phase transition. Various contributions to the specific heat have been separated. It was shown that the magnon contribution can be described satisfactorily within the model proposed for anisotropic antiferromagnets,²⁹ which confirms the presence of a large magnetic anisotropy in the cobalt sublattices. At low temperatures (below 10 K), the presence of the

Schottky anomaly related to thermal excitations of magnetic R ions to split states of the ground multiplet have been observed. Based on the analysis of this anomaly for the gadolinium ions insensitive to the crystalline field, performed within the molecular field approximation, the strength of the molecular field related to the R -Co exchange interactions in the $R\text{BaCo}_2\text{O}_{5.5}$ compounds was estimated to be ~ 1 T. It was found that at low temperatures the magnetic moments of the R ions polarize under influence of the exchange interactions with the antiferromagnetically ordered cobalt sublattices but a spontaneous magnetic ordering in the R sublattice does not appear down to 2 K.

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