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Observation of low, intermediate, and high spin states in $GdBaCo_2O_{5.45}$

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The magnetic and electrical transport properties and relative thermal expansion measurements on $GdBaCo_2O_{5.45}$ show the existence of a stabilized intermediate spin state of Co^{3+} in the temperature region $108\ K \leqslant T \leqslant 365\ K$. A charge ordering effect at 242 K due to Jahn-Teller effect followed by a ferromagnetic transition is observed in the intermediate spin state. Thermal expansion data reveal second and first order phase transitions at 163 and 359 K, respectively. These are explained as due to spin state transition accompanied by a change in the ionic radius of Co^{3+} in different spin states.

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The discovery of colossal magnetoresistance (CMR) in manganese perovskites has triggered studies in other related transition metal oxide systems, one of such compounds being $RBaCo_2O_5$, where R = rare earth element. Compared to the conventional CMR manganites, the cobaltites $RBaCo_2O_5$ can have Co-O octahedra, square pyramid or both structure depending on the amount of oxygen present.[1,2] These compounds are also excellent candidates to study the effect of spin state transitions, that are not seen in manganites, due to the ability of Co^{3+} to acquire different spin states. Another interesting feature of these compounds is the variation of the properties due to different oxygen stoichiometry. The transition of Co^{3+} from low spin [(LS) $t_{2g}^6\ e_g^0$] to intermediate [(IS) $t_{2g}^5\ e_g^1$] and high spin [(HS) $t_{2g}^4\ e_g^2$] states has been reported,[3–8] and in some compounds an associated metal-insulator transition is also observed.[6,7,9] However, the dynamics of the transition from low to high spin state is not very clear and a coherent picture of the interrelation between the structure and property has not yet emerged. In order to gain insight into the nature and effect of the spin state transitions, a detailed study on $GdBaCo_2O_{5.45}$ was done. We observed that the compound has distinct and stable low, intermediate, and high spin states with two magnetic transitions along with an antiferromagnetic and a ferromagnetic phase transition in the IS state and a IS-HS spin state transition at the metal-insulator transition temperature. Thermal expansion of the compound shows anomaly due to the spin state transitions. These results are interpreted in terms of different spin states of cobalt and are consistent with the theoretical predictions by Korotin *et al.*[10]

Polycrystalline samples of $GdBaCo_2O_{5.45}$ were prepared according to the method in Ref. 3. Stoichiometric amounts of Gd_2O_3, $BaCO_3$, and CoO powders were thoroughly mixed and calcinated at a temperature of 1000 °C. The mixture was reground, pressed into pellets and fired at a temperature of 1100 °C for 24 h. We have not explicitly determined the oxygen content, but since some of the result agrees with published data[3] we consider the oxygen content as 5.45. In order to see the effect of oxygen stoichiometry, $GdBaCo_2O_5$ is prepared in Ar following the method of Kim *et al.*[3] X-ray powder diffraction (XRD) of the samples showed formation of single phase compounds. Room temperature XRD measurements were done by a Rigaku diffractometer and Cu$K\alpha$ radiation and refinement of the diffraction data was done using the Rietveld powder diffraction profile fitting technique. Magnetization and electrical resistivity was measured by Quantum Design SQUID magnetometer and four probe method respectively in the temperature range of 5–400 K. Relative thermal expansivity was measured using high resolution capacitance dilatometry method[11] in the temperature range of 77–380 K.

Powder XRD patterns show that $GdBaCo_2O_{5.45}$ crystallizes in an orthorhombic structure with a space group of $Pmmm$ and $Z=2$. The lattice spacing are $a=3.878(5)$ Å, $b=7.831(2)$ Å, and $c=7.535(3)$ Å. There are two occupations for Co cations, i.e., Co^{I} at $2q$ crystal position and Co^{II} at $2r$ crystal position. Two kinds of Co-O clusters centered at Co^{I} and Co^{II} coexist in this structure and forms the layer structure with $Co^{I}O_6$ octahedron/$Co^{II}O_5$ square pyramid in alternate order. The distortions of these two cluster have been investigated by study of the Co-O bond lengths and Co-O-Co bond angles according to the structural refinement. The results have been listed in Table I. $GdBaCo_2O_5$ also crystallizes in an orthorhombic structure with the same space group of $Pmmm$ and $Z=1$. However, the lattice parameters and ions occupation were found to be changed, and the volume of the unit cell is around half of $GdBaCo_2O_{5.45}$. The lattice spacings are $a=3.916(0)$ Å, $b=3.923(2)$ Å, and $c=7.513(0)$ Å. There is only one occupation for Co cation and it induces only CoO_5 cluster being in this structure. However, the size of CoO_5 shows an increase along all the three inequivalent Co-O bond lengths and a bending of Co-O-Co bond angle from 162.4° (in $GdBaCo_2O_{5.45}$) to 160.97°.

Figures 1(a)–1(f) shows the field cool magnetization versus temperature data of $GdBaCo_2O_{5.45}$ at an applied field of 500 G. As shown in Fig. 1(a), six regions with different magnetic and spin states are identified and are explained below.

(i) In the low temperature region ($T \leqslant 108$ K) the magnetization exhibits a paramagnetic behavior. We tentatively assign this behavior as due to Gd and in the discussion section we will show that this is indeed the case.

(ii) Around 108 K a change in slope is seen in the M vs T curve that indicates a magnetic phase transition [Fig. 1(b)]. This phase transition is most likely due to the spin state transition of Co^{3+} from low spin ($t_{2g}^6 e_g^0$) to intermediate spin ($t_{2g}^5 e_g^1$) state.

TABLE I. The refined structural parameters, coordination of Co and ionic occupations, the distortion of CoO_6 octahedra and CoO_5 square pyramid in $GdBaCo_2O_{5.45}$ and $GdBaCo_2O_5$.

samples	$GdBaCo_2O_{5.45}$	$GdBaCo_2O_5$
S.G.	$Pmmm$	$Pmmm$
Z	2	1
a(Å)	3.878(5)	3.916(0)
b(Å)	7.831(2)	3.923(2)
c(Å)	7.535(4)	7.513(0)
v(Å^3)	228.8(7)	115.4(2)
	Ionic occupations	
Ga^{3+} $2o$ (1/2,y,1/2)	y, 0.2735(9)	$1h$ (1/2,1/2,1/2)
Ba^{2+} $2p$ (1/2,y,0)	y,0.2501(8)	$1f$ (1/2,1/2,0)
Co^{I} $2q$ (0,0,z)	z,0.2516(2)	$2q$: z, 0.2640(5)
Co^{II} $2r$ (0,1/2,z)	z, 0.2431(8)	
O^{I} $1a$ (0,0,0)		$1a$ (0,0,0)
O^{II} $1e$ (0,1/2,0)		$2r$ (0,1/2,z): Z,0.3155(0)
O^{III} $1g$ (0,1/2,1/2)		$2s$(1/2,0,z): z, 0.3224(8)
O^{IV} $2s$ (1/2,0,z)	z,0.2073(7)	
O^{V} $2t$ (1/2,1/2,z)	z,0.1920(3)	
O^{VI} $4u$ (0,y,z)	y,0.2502(1) z,0.1980(9)	
R_p	4.7%	2.7%
R_{wp}	5.9%	3.6%
s	1.1	1.4
CoO_5 square pyramid distortion [Co-O(Å) N and Co-O-Co(°) N]		
Co^{II}-O	1.977, 2	1.999,2
Co^{II}-O	1.985, 2	2.007,2
Co^{II}-O	1.832, 1	1.984,1
⟨Co-O⟩	1.951,5	1.999,5
⟨O-Co-O⟩(deg.)	162.41, 5	160.97, 5
CoO_6 octahedron distortion [Co-O(Å) N and Co-O-Co(deg.) N] of $GdBaCo_2O_{5.45}$		
Co^{I}-O	1.968, 2	
Co^{I}-O	2.001, 2	
Co^{I}-O	1.872, 1	
Co^{I}-O	1.896, 1	
⟨Co-O⟩	1.951,6	
⟨O-Co-O⟩(deg.)	166.33,6	

(iii) A second transition is observed at 165 K within the IS state of Co^{3+} [Fig. 1(c)]. Korotin *et al.* have theoretically predicted the presence of two magnetic states in the IS state and one of the states is associated with a change in the lattice parameter.[10] In accordance with the theoretical result, we associate this transition as the second magnetic state.

(iv) In the IS state the Co^{3+} undergoes an antiferromagnetic arrangement with a Néel temperature of 242 K. The magnetization then increases and the compound exhibits a ferromagnetic behavior in the temperature range $242\ \mathrm{K} \leqslant T \leqslant 279\ \mathrm{K}$ with $T_C = 279\ \mathrm{K}$ [Fig. 1(d)].

(vi) With increasing temperature another transition is seen at 365 K. This is shown in Fig. 1(e) and is probably due to the spin state transition of the Co^{3+} from intermediate to high spin state.

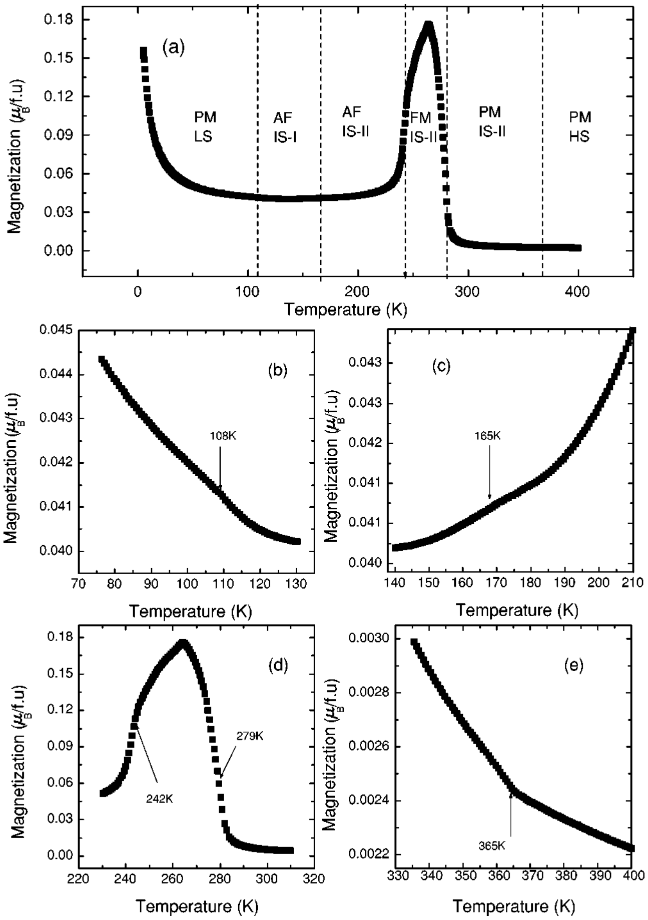

FIG. 1. (a) Field cool magnetization vs temperature curve of $GdBaCo_2O_{5.45}$ at 500 G. Dotted lines separate different magnetic and spin states. (b), (c) LS-IS state transition. (d) Antiferromagnetic and ferromagnetic transitions. (e) IS-HS state transition.

Figure 2 shows the resistivity versus temperature curve at zero applied magnetic field. The compound shows insulating behavior till 325 K except at 242 K, where the resistivity undergoes a slope change. Since this temperature coincides with the Néel temperature in the magnetization curve, we interpret, similar to the manganite case, the anomaly in the resistivity at 242 K as most likely due to charge ordering effect.[6,7,9,12] The resistivity then decreases abruptly around 325 K and a metal insulator (M-I) transition is observed at a temperature of 365 K. The absolute value of resistivity decreases from 0.01 Ωcm at 300 K to 0.00083 Ωcm at 365 K. Since the magnetization shows a IS to HS transition at the same temperature, so the M-I transition seems to be accompanied by a change in the spin state of Co^{3+}. We mention here that as shown in Fig. 2 inset, the anomaly at 242 K vanishes when a field of 5 T is applied thereby indicating the "melting" of the charge ordered state due to application of field, a fact well documented for manganites.[12] However the magnetic field does not affect the M-I transition temperature.

The relative thermal expansion of the compound in the temperature range of 77–220 K and 300–380 K is shown in

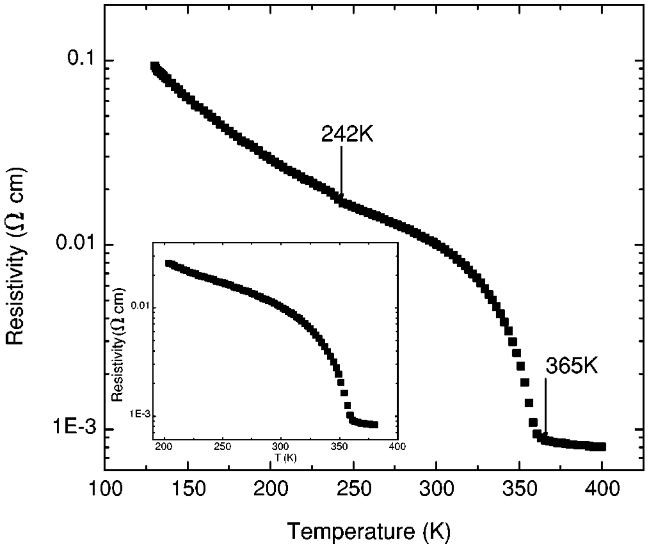

FIG. 2. Zero field resistivity versus temperature curve. The inset shows the resistivity versus temperature curve at a field of 5 T.

Figs. 3(a) and 3(b), respectively. Two distinct transitions are observed at 163 and 359 K. As shown in Fig. 3(a), the expansion curve shows a variation of slope around 163 K indicating a second order phase transition. This transition is due to the second magnetic state (within IS state) and might involve change in the lattice parameter. However to ascertain this, a detailed XRD analysis around this temperature is needed. It seems that the process of transition from LS to IS that started at 108 K completes at this temperature (163 K). A step change seen at 359 K [inset of Fig. 3(b)] indicates that the phase transition is of first order. Comparing this temperature with the IS-HS transition temperature and M-I transition temperature, we assign the transition as due to change of the spin state from intermediate to high spin state. Abrupt changes in the lattice parameters at the IS-HS transition temperature in $TbBaCo_2O_{5.5}$ have been observed by Moritomo *et al.*[6] also. To the best of our knowledge this is the first report on the anomalous behavior of expansivity in $GdBaCo_2O_{5.45}$ due to spin state transition.

From the above experimental results, it can be concluded that the magnetic properties of $GdBaCo_2O_{5.45}$ compound depend largely on the spin state of the Co ion. Magnetization versus temperature measurements of $GdBaCo_2O_5$ show that the compound exhibits a paramagnetic behavior in the entire temperature range of 5–400 K [Fig. 4(a)] and does not show any long range ordering. One of the reasons might be the fact that the average Co-O bond length increases from 1.951 Å in $GdBaCo_2O_{5.45}$ to 1.999 Å in $GdBaCo_2O_5$ and the average Co-O-Co bond angle decreases from 164° to 160°. This results in a weakening of the magnetization and a paramagnetic behavior is observed. Also there is a decrease in the Co^{3+} content in $GdBaCo_2O_5$ that results in a weakening of the magnetization. However, magnetization versus field measurement at 2 K [Fig. 4(a) inset] reveals that the magnetization tends to saturate in the paramagnetic region with maximum magnetization almost same for both $GdBaCo_2O_{5.45}$ and $GdBaCo_2O_5$. We estimate that for $H \rightarrow \infty$ the magnetization value will be $7.83\mu_B$/f.u. and $7.25\mu_B$/f.u. for $GdBaCo_2O_{5.45}$ and $GdBaCo_2O_5$, respectively, which is very close to the moment of free Gd^{3+} ion. This leads us to the conclusion that at low temperature the observed moment is primarily due to Gd^{3+} that acts as a noninteracting paramagnet in the otherwise antiferromagnetic Co sublattice. It may be noted here that at low temperature the Co is in low spin state and as such has no magnetic moment. Hence there is no contribution from Co in the low temperature region. In $YBaCo_2O_5$, since Y is nonmagnetic, no paramagnetic behavior is observed in the low temperature region,[4] a fact that supports our conclusion. On the other hand $SmBaCo_2O_{5.45}$ (Ref. 7) exhibits a fairly large magnetization even at the low temperature thereby indicating the possibility of Co^{3+} in intermediate spin state rather than in low spin state. However in $GdBaCo_2O_{5.45}$ due to a nonunity ratio of Co^{3+} and Co^{2+} there are more numbers of Co^{3+} in octahedral sites, some of which might retain their high spin state even at the lowest temperature. This might be a possible explanation for a slightly higher moment of $GdBaCo_2O_{5.45}$ as compared to

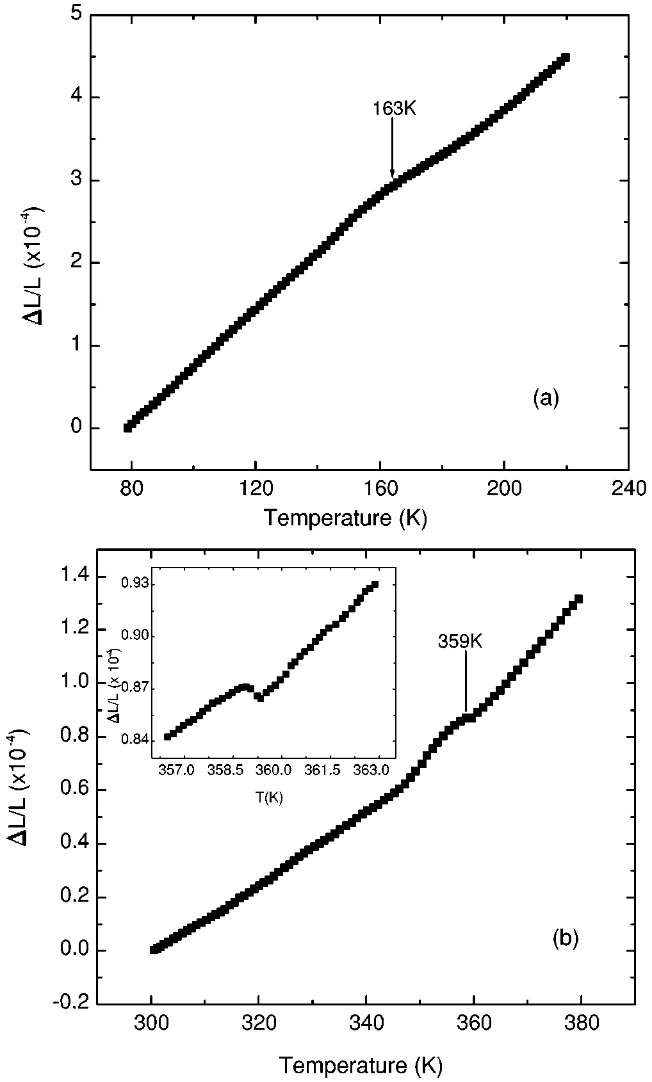

FIG. 3. (a) Relative thermal expansion curve from 77–220 K. (b) Relative thermal expansion curve from 300–380 K. The inset shows the step change in the expansion curve at 359 K.

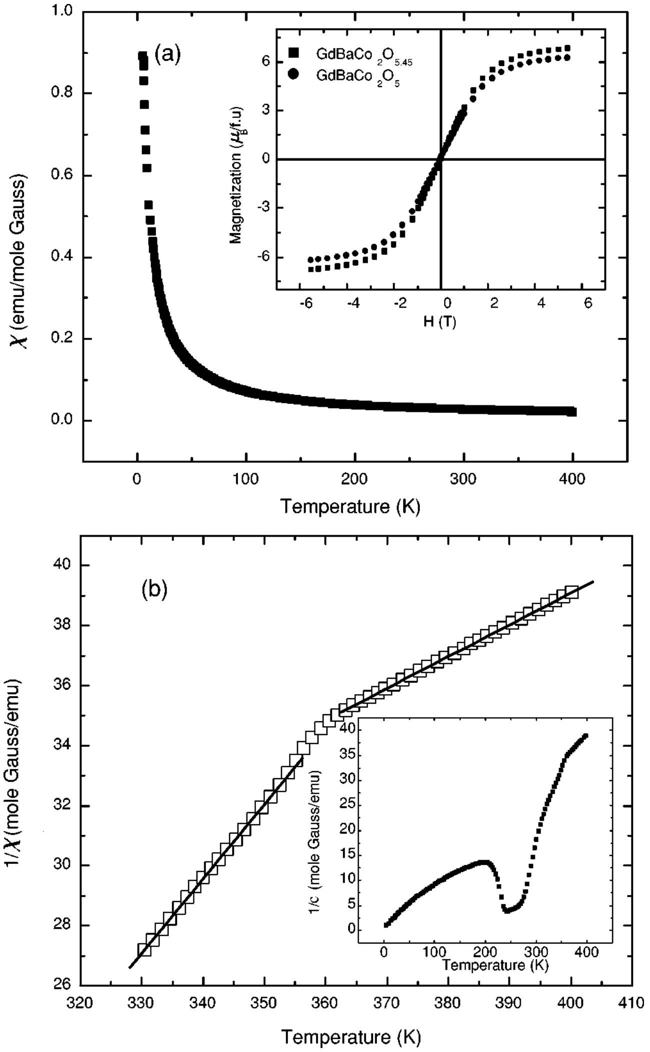

FIG. 4. (a) Field cool magnetization vs temperature curve of $GdBaCo_2O_5$ at 500 G. The inset shows magnetization vs field curve at 2 K for $GdBaCo_2O_5$ and $GdBaCo_2O_{5.45}$. (b) Inverse susceptibility curve of $GdBaCo_2O_{5.45}$ in the temperature region 330–400 K. The straight line shows the Curie-Weiss fit to the curve. Inset shows the inverse susceptibility curve from 5–400 K.

$GdBaCo_2O_5$ at 2 K. In the low spin phase of Co^{3+} the e_g orbital is empty and a strong t_{2g}-p_π-t_{2g} bonding component between Co $3d$ and O $2p$ dominates over the e_g-p_σ-e_g bond resulting this state to be an insulator.

Based on the magnetization of $GdBaCo_2O_5$ and $GdBaCo_2O_{5.45}$, it can be assumed that the spin state of Co^{2+} and Co^{3+} ions in the pyramidal site do not change with temperature, in contrast to the Co^{3+} ions present in the octahedral site that has a temperature dependent spin state. With increase of temperature the t_{2g} electrons of Co^{3+} get thermally excited and an electron is transferred to e_g level resulting in a stable IS state ($t_{2g}^5 e_g^1$) which is Jahn-Teller (JT) active. At the charge ordering temperature, usually there is an increase in resistivity and changes along the crystallographic *a*, *b*, and *c* axes.[12] Thus the charge ordering is most likely associated with the Jahn-Teller distortion. In the present case, the charge ordering takes place at a temperature where Co^{3+} is in the JT active state. From our structural data also we have found that there is a difference in the Co-O bond length in among the octahedral and square pyramid sites. This difference is most likely due to the JT effect and the distortion of the octahedra and the pyramidal sites can be a source of the ordering of charges. In the compound $GdBaCo_2O_{5.45}$ the structure is such that there is an alternation of the octahedral and pyramidal structure that extends towards the *a* axis [see Fig. 1(b) of Ref. 5]. Considering a two sublattice model, along the *b* direction the spins are aligned in the same direction. Along the *a* and *c* direction the spins are aligned in the opposite direction resulting in an antiferromagnetic interaction in the *ac* plane. Therefore along the *a* direction there is an alternation of the spin direction among the neighboring octahedral and square pyramid site. It may be noted that such a spin structure supports the fact that there is in-plane ferromagnetic interaction and interplane antiferriomagnetic interaction. Korotin *et al.*[6] have calculated that such a charge ordering state reduces the entire electronic energy and is therefore a preferable state. Spin arrangements of similar kind are also reported by Fauth *et al.*[8] who also report a structural change and appearance of additional superstructure peaks below the charge ordering temperature. However, since Ref. 8 deals with $R\mathrm{BaCo_2O_5}$ so the structure is square pyramid only. Nevertheless, this does confirm the presence of a charge ordered state in the IS state of Co^{3+}. Application of magnetic field destroys (“melts”) the charge ordered state and favors ferromagnetism. There exists a competition between the in-plane ferromagnetic interaction and the interplane antiferromagnetic interaction and at around 242 K the ferromagnetic interaction overcomes antiferromagnetic superexchange interaction thereby establishing a long range ferromagnetic state with $T_C = 279$ K.

The temperature induced spin state transition to HS state takes place in the paramagnetic region at 365 K. In Fig. 4(b) we have shown a Curie Weiss fit to the experimental data points and the inset shows the inverse susceptibility from 5–400 K for $GdBaCo_2O_{5.45}$. Two distinct linear regions are identified each with an effective moment of $8.85\mu_B$/f.u. and $5.67\mu_B$/f.u. for $T > 365$ K and $T < 365$ K, respectively. Since the effective paramagnetic moment of Gd cannot change, the only reason for the change of moment by $3.18\mu_B$/f.u. could be accounted for is by considering a change of the Co^{3+} spins from intermediate to high spin state. A similar result is reported by Moritomo *et al.* for $TbBaCo_2O_{5.5}$ compound[6] although their effective moment per Co^{3+} ion does not seem correct. Also the assertion that this transition could be due to low-spin–intermediate-spin transition of Co^{3+} in octahedral site[7] seems not correct as the Co moments values are much higher. The HS state ($t_{2g}^4 e_g^2$) is Jahn-Teller (JT) inactive. Thus there is a change over from JT active to JT inactive state resulting in the reduction of electron-lattice coupling and a transition from localized to (at least partially) itinerant Co $3d$ electron is realized. Also due to a change in the electron-lattice coupling a change in the lattice structure should be observed which is consistent with our thermal expansion result.

The anomalies in the relative thermal expansion curve represent phase transitions due to the spin state transition. The ionic radius of Co^{3+} is different in LS and HS state (LS: 1.89 Å and HS: 1.95 Å).[13,14] Due to the transition in the IS state at 163 K, the ionic radius of Co^{3+} changes. The oxygen ions surrounding the Co^{3+} move cooperatively in order to adjust for the size change causing the lattice to expand. However the resulting change in the Co-O distance is very feeble. There is no discontinuity in the structure as is evident from the smooth slope change in the thermal expansivity curve [Fig. 3(a)]. On the other hand, comparing the result of x-ray diffraction on $TbBaCo_2O_{5.5}$,[6] the first order transition at 359 K [see Fig. 3(b)] indicates a structural change due to IS-HS state transition of Co^{3+}. Due to a larger ionic radius of Co^{3+} in the HS state, along with the oxygen, most probably the Gd (Ba) ions also suffer a displacement. The octahedra and the square pyramids therefore get distorted. In the insulating state ($T<365$ K), most likely the average Co-O bond increases along the b axis, and contracts along the c axis, although the amount of distortion in the individual octahedral and pyramidal sites might not be same. Since the the $3d$-$2p$ overlap is determined by the Co-O distance, change in the Co-O distance affects the p-d interaction. The distortion causes the Co-O-Co bond angle and the band width to decrease. In the $T>365$ K region, the p-d interaction increases along with a reduction in the distortions of the octahedra and the square pyramid structure. From the experimental results it seems that in the insulating region overall effect of these competing forces is to destabilize the double exchange interaction and increase of charge localization resulting in an insulating state. As has been reported in Refs. 6,7 and also mentioned above, the distortion in the octahedral and square pyramidal Co sublattices are different and could be one of the reasons for the stabilization of these spin states.

In conclusion our results suggest that the evolution of Co^{3+} low spin to the high spin state takes place through an intermediate spin state. This state is stable and exhibits rich magnetic properties. The IS state transition makes the compound Jahn-Teller active resulting in charge ordering. An insulator-metal transition associated with a spin state transition of Co^{3+} from IS to HS state is observed. Finally it was found that the spin state transitions are accompanied by a change in the ionic radius of Co and probably also the lattice structure as is evident from the anomalies in thermal expansion measurements.

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