X-ray diffraction study of superstructure in GdBaCo₂O_{5.5}

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A single crystal of GdBaCo₂O_{5.47(2)} has been studied by means of x-ray diffraction. Below the first-order metal-insulator transition, a continuous transition to a phase with a doubled orthorhombic unit cell is discovered at T_C =341.5(7) by the appearance of very weak superstructure reflections. The critical exponent for the order parameter is found to be β =0.328(8), indicating an Ising pseudospin ordering in a 3D system. The systematic extinction of the superstructure reflections evidences the crystal symmetry change from *Pmmm* to *Pmma*, which explains the existence of a spontaneous moment. The integrated intensities are used to calculate the atomic displacements from their positions in the high-temperature phase. The cobalt-ligand distances in the ordered phase are discussed in terms of possible spin-state and/or orbital ordering of Co³⁺ ions.

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Since the discovery of giant magnetoresistivity in the oxygen-deficient layered double perovskites $RBaCo_2O_{5+x}$, where R is a rare earth,¹ these materials have attracted high interest. Their orthorhombic structure at $x \approx 0.5$ with the unit cell $a_1 \approx a_p$, $a_2 \approx 2a_p$, $a_3 \approx 2a_p$, where a_p is the pseudocubic perovskite cell parameter, is usually described by the Pmmm space group.^{2–5} One can imagine the structure as a sequence of stacking plains $[CoO_2][BaO][CoO_2][RO_r]$ along [0,0,1], which results in two types of the cobalt environment: CoO₅ pyramids and CoO₆ octahedra. The nominal valence of cobalt at x=0.5 is 3+. It is known⁶ that the Co³⁺ ion has a nonmagnetic, or low-spin ground state [(LS), $t_{2a}^6 e_a^0$, S=0], as well as two excited states, the intermediate-spin [(IS), $t_{2g}^{5}e_{g}^{1}$, S=1] and the high-spin [(HS), $t_{2g}^{4}e_{g}^{2}$, S=2]. The energy differences are small enough to gain the excited states by thermal fluctuations or due to the lattice change, which results in spin-state transitions.⁷

A metal-insulator (MI) transition has been discovered, with the transition temperature for $GdBaCo_2O_{5+r}$ 350 K < T_{MI} < 370 K being dependent on the oxygen content of 0.4 < x < 0.47.^{1,2,8,9} The transition is of the first order, which is indicated by a hysteresis of 8 K in the resistivity⁸ for TbBaCo₂O₅₄ as well as by a step change of the thermal expansion³ at T=359 K for GdBaCo₂O_{5.45}. A spin-state transition coupled with the orbital degrees of freedom is suggested to be a driving force for the MI transition. The distribution of the IS e_g orbitals $(3x^2 - r^2)$ in pyramids and $(3y^2 - r^2)$ in octahedral sites on cooling has been suggested as an origin of the transition on the basis of structural studies¹⁰ of TbBaCo₂O_{5.5}. On the other hand, it has been concluded⁴ from the structural data that the transition from an insulating to a metallic phase in GdBaCo₂O_{5.5} is due to the excitation of the LS-state electrons into an e_g band of the Co HS-state in octahedra, with Co in pyramids having IS on both sides of T_{MI} . This conclusion has been made because of an octahedron expansion of about 0.012(4) Å and a simultaneous pyramid shrinking. The density-functional-theory calculations suggest that below the MI transition $t_{2g} (xy/xz)$ orbital ordering occurs.¹¹

Spin ordering at 280–300 K has been found for a series

of RBaCo₂O_{5.5}, with a spontaneous moment existing in a narrow range just below the ordering temperature.¹²⁻¹⁴ This moment of about 0.4 $\mu_{\rm B}$ /Co is aligned along the [1,0,0] axis, as measured¹⁴ on a detwinned single crystal of GdBaCo₂O₅₅ at T=260 K. Following the arguments⁴ in Ref. 14, the Co³⁻ ions in octahedral and pyramidal sites are considered to be in the LS and the IS states, respectively, with the moments being ordered ferromagnetically along the [1,0,0] axis in one pyramidal plane (0,1,0) and antiferromagnetically between the nearest pyramidal planes. The ferromagnetic interaction in one plane is explained by the chessboardlike, or ladder order of the e_{ρ} orbitals $(3z^2 - r^2)$ and $(x^2 - y^2)$. In Ref. 12, the neutron-diffraction data for the Ho(Tb) materials have been explained by the ordering of LS and IS states in octahedra in the rows along [0,0,1] alternating in the [1,0,0] direction, with all pyramidal Co^{3+} ions being in the IS state.

All models of spin-state and/or orbital ordering mentioned above should result in distortions of the coordinating oxygen polyhedra and, as a consequence, in superstructures due to the atomic displacements (see Ref. 15 and references therein). In all of the cases, perhaps with an exception,¹¹ the superstructure should double the shortest edge \mathbf{a}_1 of the unit cell; i.e., the wave vector is¹⁶ $\mathbf{k}_{20} = (\pi/a_1)[1,0,0]$. The objective of our experiment is a search for the superstructure reflections (h/2, k, l) corresponding to \mathbf{k}_{20} that should allow, if any, to make some conclusions on the possible consequences of this ordering. The difference of the Co^{3+} electronic structure and the ionic radii are too weak effects to remarkably influence the intensities of the fundamental Bragg reflections in x-ray diffraction.¹⁷ However, the superstructure reflections, being explicitly due to atomic displacements, may give very precise data on the shape of the coordinating polyhedra that contain more information than the ionic radii themselves.

Our experience in similar investigations^{18,19} shows that superstructure reflections with the intensity of $10^{-4}-10^{-5}$ of the basic ones can be measured with a good-enough precision using a conventional x-ray tube with Ag K_{α} or Mo K_{α} radiation in the transmission geometry. A platelike crystal of the optimal thickness (about 0.07 mm and $\sim 3 \times 3$ mm² wide) allows us to measure a sufficient number of reflections, with the beam of 0.5 mm in diameter being always completely caught by the crystal. We have found that this method gives quantitative results, since all the corrections are well known, unlike resonant scattering (compare Refs. 20 and 21). No doubt, the latter is preferable in special cases, for instance, to distinguish magnetic scattering. Certainly, the measuring time in our case is much longer than with resonant scattering on a synchrotron, but the signal-tobackground ratio is good, and the time of experiment is not strictly limited as on a synchrotron. In our experiment, the x-ray beam from a 2 kW tube with a Mo anode was monochromated by a PG crystal (λ =0.71 Å). To avoid a λ /2 contamination, the high voltage on the tube was kept less than the threshold of the λ /2 excitation in the white spectrum.

 $(2 \times 2 \times 0.2 \text{ mm}^3)$ A platelike single crystal of $GdBaCo_2O_{5+x}$ with a [0,0,1] axis perpendicular to the plate was grown from the high-temperature flux melt using an off-stoichiometric mixture of corresponding oxides.⁹ The asgrown crystal was annealed for several days at 600 °C under 3 bar of oxygen pressure and then cooled down to room temperature. Twinned structures of the [1,1,0] type in the oxygenated crystals were clearly seen with the Faraday image in the normal-reflection mode. The crystal phase purity and its cationic composition were checked by x-ray diffraction and x-ray fluorescent analyses. The oxygen content in the crystal that was grown and oxygenated in the same batch was determined by iodometric titration to be 5.47(2). The magnetic and transport properties were investigated for a similar crystal. In agreement with Refs. 9 and 14, the magnetization data clearly show significant anisotropy of the magnetic response. The spin-ordering transition at $T_N \approx 275$ K to the phase with a spontaneous moment is followed by a second transition at $T \approx 250$ K to a purely antiferromagnetic phase and then by a third transition around T \approx 150 K to another antiferromagnetic state. The first-order MI transition reveals at $T_{MI} \approx 365$ K in the resistivity and the magnetization.

The crystal was mounted on four-circle diffractometer, and the thermocouple was safely stuck together with the crystal to ensure a good thermal contact. The temperature difference between the thermocouple and the sample was not more than 0.5 K. The temperature was changed in the range of 130-440 K by means of a nitrogen-gas flow with a temperature stability better than 0.5 K.

A number of weak superstructure reflections (Fig. 1) due to unit-cell doubling were observed at room temperature. The twinning is shown schematically on the reciprocal lattice inset in Fig. 1. The indices (h, k, l), with h being odd for the superstructure reflections, refer to the unit cell $(2\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$. However, a wide x-ray beam used for luminosity improvement spoils the resolution, and the reflections (hkl), (khl)cannot be resolved, since $2a_1 \approx a_2$. Therefore, only the superstructure reflections with odd h and k are not superimposed onto the fundamental ones. With the resolution available, all the spots resulting from splitting of a reciprocal-lattice point participate in a single Bragg peak, and one has to average properly over different twins when processing the data. Poor resolution is also a reason to choose the lattice parameters



FIG. 1. A scan along [h,h,0] through the superstructure reflection (3,1,1). The insert shows schematically the twins for a reciprocal lattice layer $l \neq 0$. The fundamental and the superstructure points are described by big and small circles, respectively.

 a_1 =3.87 738 Å, a_2 =7.82 690 Å, a_3 =7.53 487 Å from Ref. 2 for the orientation matrix.

The condition of capturing the entire beam to obtain a quantitative set of integrated intensities restricted the number of independent superstructure reflections to 24. All of them as well as the 11 fundamental ones were measured at room temperature by means of the $\theta - 2\theta$ scans. Unfortunately, because of the crystal's fragility, we failed in decreasing the crystal thickness to the optimal value, and the transmission was rather low, varying from 10^{-2} to 5×10^{-3} for the reflections measured. Nevertheless, with the thickness dispersion of our crystal being about 5×10^{-3} mm, the precision of the transmission correction [Eq. (8), Ref. 22] was about 3%. The low transmission simply increased the counting time. To get reasonable statistics the counting time in each point when scanning across the superstructure peaks was equal to 900 s, whereas a total scan across the strongest fundamental peak took about 30 s. A typical scan is shown in Fig. 1. It is worthwhile to note that the average intensity of the superstructure reflections is 2-4 orders of magnitude less than that of the fundamental ones, and it is very sensitive to spurious effects. This is why all of them were checked by rotation around the scattering vector for possible contribution of multiple scattering or occasional reflections from small crystals of erroneous phases.

The temperature dependence of the integrated intensity of the superstructure peak (3,1,1) is shown in Fig. 2. A change of the peak width was not detected. Having a precision of the sample temperature better than 1 K as indicated above, one can conclude that the superstructure reflections appear about 25 K below the metal-insulator transition, even if T_{MI} varies among the crystals from the same batch. Moreover, the new transition is continuous, while the MI one is of the first order, as mentioned above. Hence, we conclude that an additional second-order transition with $\mathbf{k}_{20} = (\pi/a_1)[1,0,1]$ is discovered in between T_{MI} and T_N .

The temperature dependence of the intensity shown in Fig. 2 was corrected for the critical, diffuse scattering, using the intensities above the critical point T_C and assuming the ratio of the critical amplitudes $C^+/C^-=2$ in the mean-field approximation.²³ Intensities thus corrected for a current criti-



FIG. 2. Temperature dependence of intensity of the (3,1,1) superstructure reflection. The insert shows the log-log plot of the intensity versus the reduced temperature τ .

cal point $T_{\rm Ci}$ were fitted by the power function $I(\tau_i) \propto \tau_i^{2\beta_i \tau_i}$, where $\tau_i = (T_{\rm Ci} - T)/T_{\rm Ci}$, and β_i is the critical exponent for the order parameter corresponding to $T_{\rm Ci}$. Then the entire procedure was repeated at another $T_{\rm Ci}$. The final values of T_C =341.5(7) K and β =0.328(8) have been chosen using criteria of the residual least-squares minimum. The value of β is in excellent agreement with β =0.325(1) for the O(1) symmetry, and there is a statistically significant difference of 4.6 standard deviations with β =0.365(1) for O(3) symmetry, as obtained from the field theory in three dimensions.²⁴ The peak intensity follows this power law down to about 280 K, i.e., roughly to the spin-ordering transition.

The agreement of β with the O(1) scenario indicates a transition, which is analogous to the ordering of an Ising pseudospin. One may assume that the superstructure reflections arise due to the atomic displacements, which presumably accompany a spin-state and/or orbital ordering. (The primary effect itself is too weak to explain their intensities.) We have tried to reconstruct this possible ordering on the basis of the atomic displacements calculated from the intensities of the superstructure reflections. Out of 24 reflections measured at room temperature, only 11 reflections with $l \neq 0$ have intensities nonequal to zero, i.e., stronger than three standard deviations. (Some very weak reflections with

l=0 were also detected, but their intensities strongly changed when the crystal was turned around the scattering vector. which evidences that they were due to multiple scattering.) This systematic extinction indicates a change of the space group. According to Ref. 25, the highest subgroup of Pmmm for the superstructure wave vector \mathbf{k}_{20} that has the extinction law observed is *Pmma* with the origin of the doubled unit cell at the point (-1/4,0,0). The atomic positions can be expressed through the mean coordinates X_i , Y_i , Z_i in the high-temperature *Pmmm* phase and the displacements x_i , y_i , z_i (Ref. 26), as shown in Table I. Unlike space group *Pmmm* where equivalent positions in the doubled unit cell at Z+zand -Z-z have the same coordinates X and Y, in *Pmma* they are transformed by the glide plane *a*, with a difference in the X coordinate being equal to $\frac{1}{2}$. This means that the same states of Co³⁺ (spin or orbital) are not arranged in the rows along [0,0,1], but are ordered in a chessboardlike manner in both the octahedral and the pyramidal planes.

The scale factor for the calculation of atomic displacements has been obtained from the basic Bragg intensities, using for X_i , Y_i , Z_i the data in Ref. 4, but there is no significant difference in the scale factor obtained with the set of data in Ref. 2. All necessary corrections of the intensity have been made for transmission (as mentioned above), polarization, and the Lorentz factor. The extinction correction²⁷ has been found insignificant even for the fundamental reflections. For the very weak superstructure reflections it is obviously negligible. The superstructure intensities were corrected in the same way, except extinction, and were used in the refinement of the atomic displacements at the fixed value of the scale factor. The contribution from the twins (Fig. 1) was assumed to be equal. The values of the displacements x_i . y_i , z_i are small, and therefore an expression for the intensity I(q) of a superstructure reflection with the Miller indices h, k, l can be simplified. Developing the structure factor into a series to the first order in displacements from the mean atomic positions X_i , Y_i , Z_i one can write

$$I(q) \propto \{ \sum 2\pi f(q)(hx_i + ky_i + lz_i) \cos[2\pi (hX_i + kY_i + lZ_i]]^2,$$
(1)

where $q = \sin \theta / \lambda$, f(q) is the atomic form factor, for X_i , Y_i , Z_i the data⁴ are used, and the sum is taken over all the atoms of

TABLE I. Distribution of atoms over the positions of the space group *Pmma*. The symbols Py1, Py2, Oc1, Oc2 are used for Co ions in the polyhedra Pyramid 1, 2 and Octahedron 1, 2. The data from Ref. 4 are used for Z(Py1)=0.2522, Z(Py2)=0.7478, Z(Oc1)=0.2561, Z(Oc2)=0.7439, Z(O1)=0, Z(O2)=0, Z(O3)=0.5, Y(Ba)=0.2500, Y(Gd)=0.2722, Z(O1)=0, X(O4)=0, Z(O4)=0.3132, X(O5)=0, Z(O5)=0.5, Y(O61)=0.2450, Z(O61)=0.2992, Y(O62)=0.2450, Z(O62)=0.7008.

Atoms	Site	1	2	3	4
2Py1, 2Py2, 2O1	2e	1/4, 0, (Z+z)	3/4, 0, -(Z+z)		
20c1, 20c2, 202, 203	2f	1/4, 1/2, (Z+z)	3/4, 1/2, -(Z+z)		
4Ba	4g	0, (Y+y), 0	0, -(Y+y), 0	1/2, (Y+y), 0	1/2, -(Y+y), 0
4Gd	4h	0, (Y+y), 1/2	0, -(Y+y), 1/2	1/2, (Y+y), 1/2	1/2, -(Y+y), 1/2
404	4i	(X+x), 0, (Z+z)	-(X+x), 0, -(Z+z)	1/2+(X+x), 0, -(Z+z)	1/2 - (X+x), 0, (Z+z)
405	4j	(X+x), 1/2, (Z+z)	-(X+x), 1/2, -(Z+z)	1/2+(X+x), 1/2, -(Z+z)	1/2 - (X+x), 1/2, (Z+z)
4061, 4062	4k	1/4, (Y+y), (Z+z)	1/4, -(Y+y), (Z+z)	3/4, -(Y+y), -(Z+z)	3/4, (Y+y), -(Z+z)



FIG. 3. Displacements of atoms in the *Pmma* phase from their mean positions in the *Pmmm* phase shown for half a unit cell. The origin is at the point (-1/4,0,0). The arrow lengths are approximately proportional to the displacements z(O11)+z(O21) = 0.011(2) Å, z(O31)=-0.008(1) Å, x(O44)=0.0304(5) Å, x(O54)=0.0437(7) Å, y(O611)=0.0011(5) Å, z(O611) = 0.031(2) Å, y(O621)=-0.0043(5) Å, z(O621)=-0.036(4) Å. The last figure of an atom number corresponds to the column number in Table I.

doubled unit cell that participate in the structure factor. For instance, the atoms of Ba and Gd should be excluded²⁶ for all reflections (*hkl*) with h=2n+1. Since X(O4)=X(O5)=0, the z displacements of these atoms do not participate in the intensity. The displacements z(O1), z(O2) cannot be distinguished and should be varied as one parameter. As a result, there are 12 independent displacements, as follows from Table I. Having the intensities of 11 superstructure reflections, we are obliged to make some reasonable assumptions. We assumed at the beginning that $|z(Py1)| \approx |z(Py2)|$ and $|z(Oc1)| \approx |z(Oc2)|$, which finally became zeros in the limits of the standard deviations, and we are left with 7 variables. The results of the refinement are shown in Fig. 3, and the agreement between the calculated and observed intensities is displayed in Fig. 4. The least-squares residual is $\chi^2 = 2.5$. Uncertainties of the variables indicated in the caption to Fig. 3 include only a standard deviation and are definitely underestimated. Nevertheless, the shifts x(044), x(054), z(0611),



FIG. 4. Comparison of the calculated (I_{calc}) and observed (I_{obs}) intensities of the superstructure reflections.



FIG. 5. Spin-state and/or orbital ordering in the octahedral (Oc11–Oc22) and pyramidal (Py11–Py22) sites. The orbitals e_g are described on the background of the t_{2g}^4 and t_{2g}^5 ones, with the former being less shadowed.

z(O621), and y(O621) should be statistically significant, even with doubled uncertainties. Using these displacements and taking into account the relations between the coordinates of equivalent atoms given in Table I, we shall try to reproduce the spin-state and/or orbital ordering, which is assumed to be the reason for the atomic displacements, as discussed above.

When analyzing the displacements in terms of possible spin-state and/or orbital ordering of the Co³⁺ ions one may consider as a crude approximation only half-filled e_{ρ} orbitals and assume that the t_{2g} ones are close to spherical symmetry. Then a ligand between two Co ions should be shifted to one with the less extended e_g orbital. Shown in Fig. 3, the shifts of the ligands x(O43) = -x(O42), z(O614) = z(O613), and, with less significance, y(O621) = -y(O622) indicate that the e_g electrons of Co³⁺ in the Py12 site should be extended in three directions; i.e., most probably there are two e_{g} orbitals, (x^2-y^2) and $(3z^2-r^2)$, resulting in the HS state, which have been observed²⁸ for Sr₂CoO₃Cl. The Co³⁺ ion in the equivalent position Py11 should have the same electronic configuration. If the shifts x(O53)=x(O51)=-x(O52)=-x(O54) as well as y(O621) = -y(O622) = -y(O623) = y(O624) are also taken into account, one may assign the e_g orbitals (x^2-z^2) and $(y^2 - z^2)$ to the Co³⁺ ions in the positions of Oc11, Oc12 and Oc21, Oc22, respectively. Finally, one has nothing to do but the assign the e_g orbital $(3z^2 - r^2)$ to Co³⁺ in the sites Py21 and Py22. The suggested spin-state and/or orbital order is described in Fig. 5 on the background of the pseudospherical t_{2g} orbital shadowed, depending of the number of electrons. Therefore, two Co⁺³ ions out of four in the pyramidal sublattice and entire octahedral sublattice are in the IS state. Apparently both the HS and IS states are mixed with the LS ground state.

The assumption³ that orbital ordering exists only in the pyramidal sites is not consistent with our results. According to Ref. 4, the octahedral Co³⁺ ions should be in the LS state below the MI transition, while in our case they are in the IS state, probably with an admixture of the LS state. From our data we can say nothing as to the t_{2g} (xy/xz) orbital ordering.¹¹

Some of the above-mentioned models of ordering can be checked even without numerical results. The ordering of LS

and HS states in octahedra¹² is described by space group *Pmmm*, while the orbital ordering in pyramids¹⁴ results in the vanishing of some superstructure reflections. Therefore, these two models can be ruled out. Another important conclusion that can be made on the basis of qualitative results concerns the nature of a spontaneous moment. Until now, the unit-cell doubling was considered to be a result of antiferromagnetic ordering with the wave vector $\mathbf{k}_{20} = (\pi/a_1)[1,0,0]$ (Refs. 12 and 13). In the unit cell, doubled because of atomic displacements, the wave vector of the magnetic structure is equal to zero, which is an obligatory condition for the appearance of a spontaneous moment. conclusion, a second-order transition In at T_{C} =341.5(7) K is discovered to a phase with the symmetry *Pmma*. The \mathbf{a}_1 edge of the high-temperature unit cell (*Pmmm*) is doubled. This superstructure explains the existence of a spontaneous moment in the magnetically ordered high-temperature phase. The atomic displacements are obtained from the intensities of the superstructure reflections. These displacements may be explained by the HS-IS ordering in the pyramidal planes, while all the Co ions in octahedral planes are in the IS state. The orbital order should be present in both the pyramidal and octahedral planes. Similar results, which will be published elsewhere, are also obtained for DyBaCo₂O_{5.5}.

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