Gigantic magnetic-field-induced polarization and magnetoelectric coupling in a ferrimagnetic oxide CaBaCo$_4$O$_7$

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Below T_C, the single-crystal study of CaBaCo$_4$O$_7$, a noncollinear ferrimagnet ($T_C = 64$ K) with a polar orthorhombic space group ($Pbn2_1$) between 4 and 293 K, shows a large change in the electric polarization along its $\vec{c}$ axis reaching $\Delta P = 17$ mC/m^2 at 10 K. At 62.5 K, a magnetic-field-driven giant variation in polarization $P(9$ T$) - P(0$ T$) = 8$ mC/m^2 is observed. Moreover, the present magnetoelectric measurements are fully consistent with the $m'm2'$ magnetic point group. This ferrimagnetic oxide, which belongs to the "114" structural family, opens an avenue for the search for new magnetoelectrics.

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I. INTRODUCTION

Numerous investigations of multiferroics have shown that two physical characteristics of these materials are of great importance in view of technological applications, the magnetoelectric coupling and the electric polarization, which should be as high as possible.[1,2] Based on these two prerequisites, improper ferroelectrics where ferroelectricity originates from a particular magnetic order are challenging for discovering new performances and understanding multiferroism. Significant coupling between magnetism and ferroelectricity was observed in a rather large number of improper ferroelectrics, but the coefficients of the tensor characterizing the linear magnetoelectric effect α_{ij} were rarely measured. The highest value of α that has been reported to date is close to $20\,000$ ps/m for Ba$_{0.5}$Sr$_{1.5}$Zn$_2$(Fe$_{0.92}$Al$_{0.08}$)$_{12}$O$_{22}$.[3] It is also observed that the magnetically induced polarization of these magnetoelectric ferroelectrics remains modest as compared to classical ferroelectrics with values generally smaller than 1000 μC/m^2 as shown, for example, for TbMnO$_3$,[4] MnWO$_4$,[5] TbMn$_2$O$_5$,[6] and Ni$_3$V$_2$O$_8$.[7] However, the multiferroic GdMn$_2$O$_5$ recently was shown to exhibit giant ferroelectricity[8,9] with $\sim$3600 μC/m^2, the largest observed value for improper ferroelectrics showing the potentialities of magnetic oxides.

The "114" CaBaCo$_4$O$_7$ cobaltite[10–12] exhibits a pure tetrahedral framework[10,11] where the CoO$_4$ tetrahedra are three-dimensionally interconnected and form a geometrically frustrated network (Fig. 1). The magnetic structure of this oxide shows that, similar to several improper ferroelectrics, which are antiferromagnets, the cobalt spins are noncollinear but different from the latter, and CaBaCo$_4$O$_7$ is ferrimagnetic below $T_C \sim 64$ K with $\vec{b}$ as the easy axis. In contrast to many improper ferroelectrics, it crystallizes in a noncentrosymmetric space group $Pbn2_1$ in the whole temperature range from 4 to 293 K with $\vec{c}$ as the polar axis. Studies on polycrystalline samples have shown that, below 64 K, the magnetic ordering induces an additional polarization,[12] suggesting the existence of improper ferroelectricity. In order to conclusively determine the nature of the magnetoelectric coupling and of the electric

polarization in this phase, a single-crystal study was necessary. Such a study is also motivated by the fact that the magnetic order in this oxide reduces the point-group symmetry to $m'm2'$, similar to several magnetoelectric boracites.[13–17] Here, we show that CaBaCo$_4$O$_7$ exhibits a high magnetoelectric coupling factor leading to a magnetic-field-driven gigantic change in the polarization near T_C. Neutron-diffraction data reveal an abrupt structural change at T_C, and it is proposed that the electrical polarization has a magnetostrictive origin.

II. EXPERIMENT

Millimeter-size crystals were grown using the floating-zone technique in a mirror furnace under air at 3.5 bars. Laue diffraction patterns showed that the single crystals exhibit the same characteristics as the polycrystalline samples with the space group $Pbn2_1$. Laue patterns were collected to obtain the geometric relation between crystal faces and the crystallographic axes. Finally, plateletlike crystals were cut with the thinnest dimension ($\sim$1 mm) corresponding to the $\vec{c}$ axis and with the largest faces (xy planes) reaching 5×5 mm. Magnetic measurements were performed with a superconducting quantum interference device magnetometer. A plate geometry capacitor connected to a LCR meter was used to perform dielectric permittivity measurements, whereas, polarization measurements were performed with an electrometer. For the magnetic measurements [$P(H)$ curves], a poling electrical field $E = 110$ kV/m was applied at 80 K (above T_C) to cool the crystal down to the measurement T. This procedure was used in order to try to obtain a single domain (monopole) prior to the measurements performed with a magnetic-field sweep rate of 10^{-2} T/s. The option of a Quantum Design system (PPMS) was used to measure the specific heat. Time-of-flight neutron-powder-diffraction experiments were performed at the Spallation Neutron Source (at Oak Ridge National Laboratory) on the POWGEN diffractometer. Data were collected between 10 and 75 K using two different center wavelengths of 1.066 and 2.665 Å covering d-spacing ranges from 0.4 to 3.20 Å and from 1.20 to 6.4 Å. Rietveld refinements were performed using the FULLPROF package.
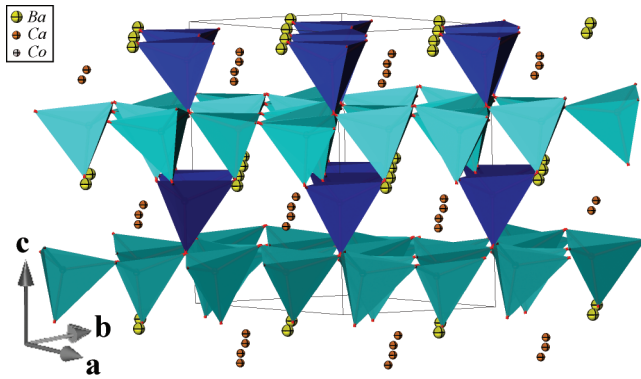
FIG. 1. (Color online) Crystal structure of CaBaCo$_4$O$_7$.

III. RESULTS

Figure 2(a) shows the field-cooled magnetization measured along the easy axis ($\vec{b}$) upon warming at 10^{-2} T. A sharp transition is evidenced with $T_C = 64$ K, in good agreement with data previously reported for the polycrystalline precursor.[10] The temperature dependence of the dielectric permittivity (ε') was measured along the $\vec{c}$ and $\vec{b}$ directions [Fig. 2(b) and inset]. Along $\vec{c}$, a clear peak is observed at T_C, supporting the possibility of a magnetoelectric coupling along $\vec{c}$ as predicted by the symmetry analysis (see Ref. 12). A second peak with no corresponding anomaly on the $M(T)$ curve was also observed at 69 K, implying a nonmagnetic origin. In contrast, along $\vec{b}$ (easy axis for magnetization), a sharp drop is observed at T_C with a small anomaly at 69 K. To test the origin of the anomaly above T_C, specific heat measurements were performed (on cooling) without and with an applied external magnetic field of 2 T using a larger crystal [Fig. 2(c)]. The peak at T_C with $\mu_0 H = 0$ becomes broader and shifts towards higher T within $\mu_0 H = 2$ T. It corresponds to the ferrimagnetic ordering. For $H = 0$, a second peak is detected at 69 K, which does not change in fields measured up to 2 T [Fig. 2(c), inset]. This strongly supports the lack of magnetic origin for this small high-temperature peak on the $\varepsilon'(T)$ curve [Fig. 2(b)].

The presence of a well-defined dielectric peak along $\vec{c}$ at T_C motivated polarization measurements. For that purpose, a thin platelet with contacts on the largest xy faces was cut from the crystal used for $M(T)$ in order to apply a small electric field along $\vec{c}$ ($E = 1.1$ kV/cm) during the cooling from 80 to 8 K. At 8 K, E was removed, and P was measured upon warming at 0.5 K/min [Fig. 2(d)]. A gigantic variation in the polarization is evidenced between 10 and 80 K. Also, the sharp transition at T_C towards $\Delta P = 0$ demonstrates the improper origin of the electric polarization in the magnetically ordered phase. However this polarization cannot be reversed completely by changing the polarity of a poling electric field ($E = \pm 14$ kV/cm). Moreover, it should be pointed out that an electric polarization is observed below T_C even in a zero poling electric field. Above T_C, the polarization remains constant (i.e., the pyroelectric current is null), but its variation cannot be measured above $\sim$150 K due to the high value of the dielectric losses.

To demonstrate the existence of a magnetoelectric (ME) coupling, P measurements were performed under a magnetic field. It must be mentioned that, with our experimental setup, no polarization measurements under both magnetic and
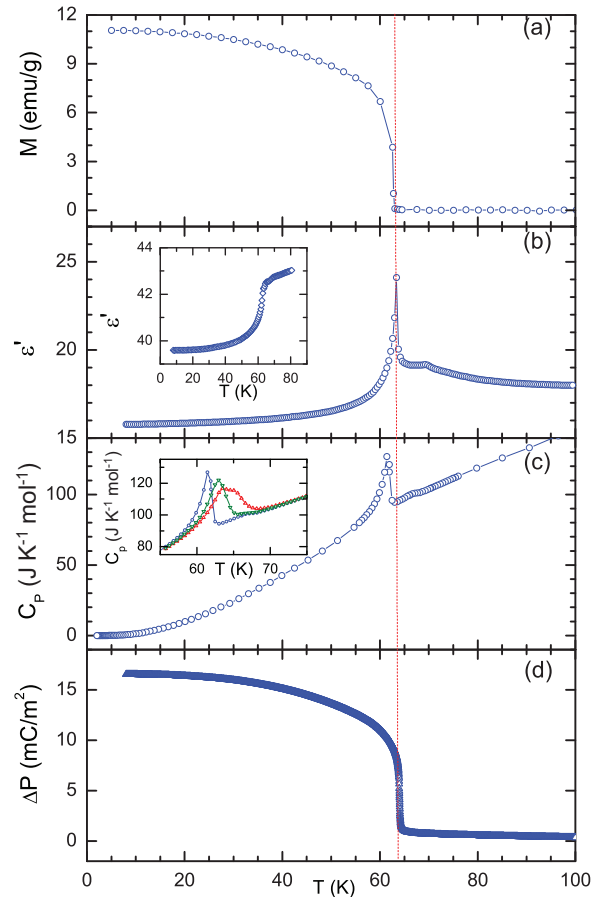

FIG. 2. (Color online) (a) Field-cooled magnetization along the b axis; Cooling and magnetic measurements were carried out under 100 Oe; (b) dielectric permittivity along the c axis at 100 kHz and along the b axis (inset); (c) specific heat and the inset of (c) shows enlargement around the T_C of specific heat measured in 0 T (blue dots), 1 T (green down triangles), and 2 T (red up triangles); (d) variation in the polarization along the c axis after poling under $E_c = 1.1$ kV/cm. All the measurements were performed upon heating, except the specific heat measurement.

electric fields could be performed. So, the coupling terms γ_{xyz}, linear in H and E and allowed in the ordered magnetic state,[12] could not be determined. Moreover, considering the anisotropic shape of the crystals, the P measurements were performed only along the thinnest direction $\vec{c}$, which is also the polar axis. In that geometry, upon application of an external magnetic field H, the induced polarization along the $\vec{c}$ axis is given by $P_z = a_{32}H_y + (b_{311}H_x^2 + b_{322}H_y^2\,b_{333}H_z^2)/2$ [Eq. (1)], where α_{ij} is the coefficient of the linear magnetoelectric tensor and β_{ijk} is the coefficient of the bilinear magnetoelectric susceptibility tensor. Applying H along $\vec{b}$, the formula reduces to $P_z = a_{32}H_y + b_{322}H_y^2/2$ [Eq. (2)] from which the two coefficients α_{32} and β_{322} can be extracted below T_C, whereas, above T_C, only β_{322} is allowed. As aforementioned, H was applied along the easy axis $\vec{b}$ in order to be perpendicular to E ($\vec{c}$ axis). The induced polarization P_z was recorded from 0 to 9 T at several temperatures between 10 and 75 K, i.e., below and above T_C. An increase in the polarization with the applied field is observed whatever the temperature in this range (Fig. 3). The values of α_{32} and β_{322}
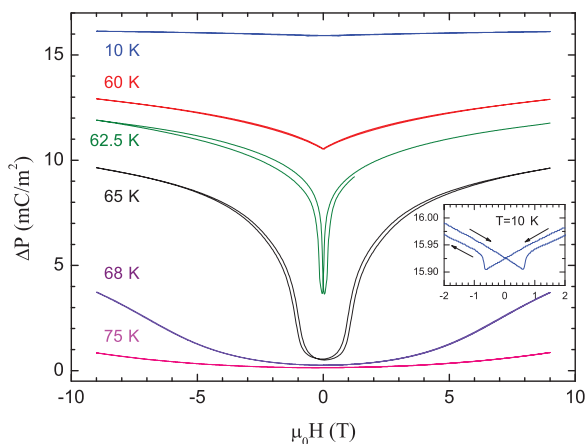
FIG. 3. (Color online) Magnetic-field dependence of the polarization along the c axis at various temperatures. The magnetic field is applied along the b axis. Inset: $P(H)$ butterflylike curve measured at 10 K.

coefficients as a function of T, obtained by fitting the $P_z(H_y)$ curves (inset of Fig. 4) between -3 and 3 T with Eq. (2), are given in Fig. 4.

From these curves, it is clear that the temperature dependence of α_{32} goes through a maximum just below T_C as observed for the Ni-Cl or Co-I boracites.[13,15] At 60 K, the value of the coefficient of the tensor α_{32} for the linear ME coupling, obtained by fitting the $P_z(H_y)_{T=60K}$ curve as shown in Fig. 4, reaches an $\alpha_{32} = 764$ ps/m value in SI units. This compares with the value of $\alpha_{xy} = 730$ ps/m reported at 1.5 K for a TbPO$_4$ single crystal.[18] As expected for the paramagnetic state, α_{32} is found to be close to zero for $T > T_C$. The bilinear coefficient β_{322} is negative below T_C and positive above T_C. Near the magnetic transition, β_{322} decreases abruptly towards negative values, changes sign at the transition, and decreases again with temperature (Fig. 4). A similar behavior has previously been measured in Ni-Cl boracites.[13] Additional measurements were also performed to verify the predictions coming from the $m'm2'$ point group. Under application of H along $\vec{c}$ (H_z), the
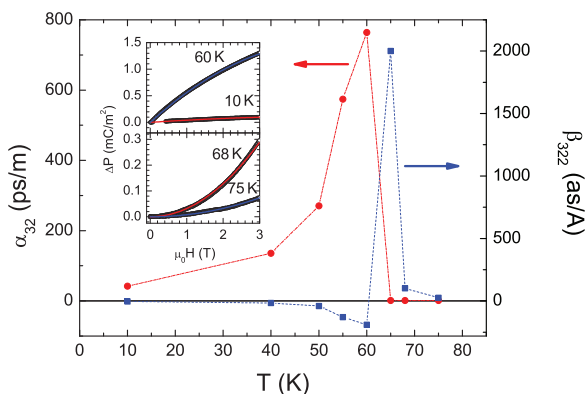

FIG. 4. (Color online) Linear magnetoelectric coefficient α_{32} (dots) and bilinear magnetoelectric coefficient β_{322} (squares) versus T in *Système International* (SI) units (dotted lines are guided for the eyes). Inset: Least-squares fit of $P_z(H_y)$ above (bottom) and below (top) T_C. For clarity, the figure shows only the fit between 0 and 3 T. At $T = 65$ K, the fit of $P_z(H_y)$ is performed between -1 and $+1$ T.

induced polarization P_z should only depend on β_{333} with $P_z = b_{333}H_z^2/2$ since the linear magnetoelectric coefficient α_{33} is expected to be equal to zero by symmetry. At 10 K, the $P_z(H_z)$ curve leads to $\beta_{333} = 18.4(2)$ as/A and $\alpha_{33} = 0.07(11)$ ps/m, i.e., $\alpha_{33} \approx 0$, as expected for the point group $m'm2'$. Thus, the present ME$_H$ measurements with H along $\vec{b}$ and $\vec{c}$ confirm the magnetic point group $m'm2'$ for CaBaCo$_4$O$_7$. As toroidization is allowed in this point group,[12] CaBaCo$_4$O$_7$ may also be ferrotoroidic. In that respect, the divergence of $\alpha_{32}(T)$ near T_C is an indirect method to probe the existence of a toroidal moment.[19] The shape of the $\alpha_{32}(T)$ curve for CaBaCo$_4$O$_7$ is consistent with the theory (for a review, see the references in Refs. 18 and 19). In addition, at $T = 10$ K, a butterfly loop in the $P(H)$ curve is observed (inset of Fig. 3) with a characteristic symmetric minimum, corresponding with the coercive magnetic field (~ 0.6 T) and consistent with a spontaneous magnetization as for LiCoPO$_4$ (Ref. 20) and a Ni-I boracite.[21]

As shown in Fig. 3, the largest ME effects are achieved close to T_C. This motivated the measurements of H-dependent M, ε', and ΔP at 65 K (Fig. 5). A large magnetodielectric effect of 80% is found in only 1 T [$\varepsilon'(H)$, Fig. 5(b)] together with a large magnetoelectric response $\Delta P(H)$ (Fig. 3). This can be compared to the derivative of the magnetization with respect to magnetic field [inset of Fig. 5(a)], showing a maximum at ~ 1–1.5 T. A metamagnetic transition occurs from a paramagnetic state below $\mu_0 H \sim 1$ T towards an ordered magnetic state above that value. This transition is reflected by the derivative curve of $\Delta P(H)$ [right inset, Fig. 5(b)] and is confirmed by the value of magnetoelectric coefficients (linear and bilinear), calculated from the $\Delta P(H)$ curve. The β_{322} coefficient is positive below 1 T as in the paramagnetic state with a value of 2.0(3) fs/A. In contrast, the β_{322} coefficient is
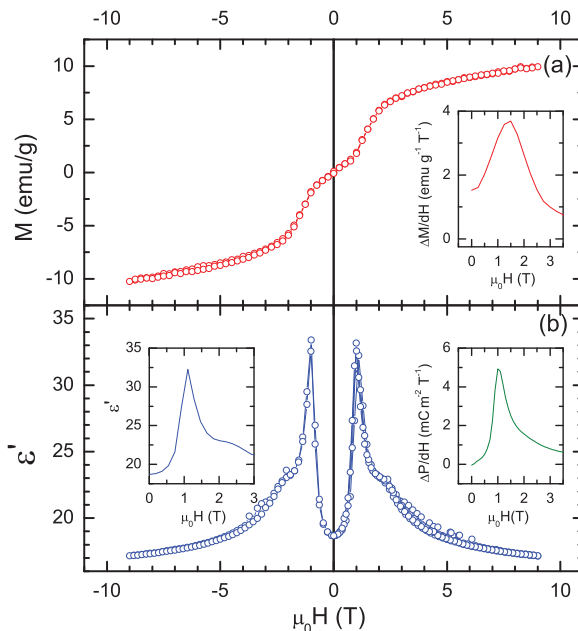

FIG. 5. (Color online) Isothermal curves collected at 65 K. (a) Magnetization versus field with $H \parallel b$; (b) magnetodielectric effect at 100 kHz versus field with $E \parallel c$ and $H \parallel b$; inset enlargements for 0 T $\leqslant \mu_0 H \leqslant 3$ T of (a) $\Delta M/dH = f(H)$ and (b) (left) $\varepsilon'(H)$ and (right) $\Delta P/dH = f(H)$.

negative above 1 T as is observed in the ferrimagnetic state below T_C. It should be pointed out that the sign change of the bilinear coefficient, i.e., the metamagnetic transition, is also observed at 68 K (Fig. 3) but under a higher field, around 7 T.

IV. DISCUSSION

Although the present measurements of pyroelectric current indicate that exceedingly high values of induced polarization are achieved in this noncollinear ferrimagnet, the lack of evidence for P switching argues that this oxide is not a ferroelectric below T_C. In the crystals, the higher ΔP values and the lack of switching as compared to the polycrystalline sample[12] suggest that large polar domains encountered in the former are prerequisites to explain these differences, or alternatively, that subtle changes in stoichiometry, in the limit of accuracy of structural refinements from neutron-diffraction data, have a strong impact on the physical properties. Nevertheless, the magnetoelectric effects measured for the crystals are remarkable. The variation in the polarization under a magnetic field reaches values as high as $\sim$8 mC/m^2 around T_C between 62.5 and 65 K, which is nearly twice the largest variation among the known magnetoelectric compounds.[8] Also, the present results suggest that exceedingly high values of induced P in the magnetic state can be achieved in noncollinear ferrimagnets.

We now consider possible origins for the high values of ΔP and magnetoelectric coupling coefficients. Different mechanisms have been invoked to explain improper ferroelectricity in centrosymmetric materials: spin spiral magnetic order, which breaks the inversion symmetry,[22] and asymmetric exchange as in a chain of alternating magnetic ions with antiferromagnetic and ferromagnetic exchanges.[23] The case of some boracites and CaBaCo$_4$O$_7$ differs from these examples

as the latter compounds are polar by symmetry with a possible electric polarization in their paramagnetic states. They exhibit an extra polarization in their ordered magnetic states and a magnetoelectric coupling resulting from the $m'm2'$ point group. However, ΔP and α values are much higher in the case of CaBaCo$_4$O$_7$ as compared to magnetoelectric boracites. Moreover, since the variation in the polarization and the values of the magnetoelectric coefficients are at their maximum near T_C, the magnetostriction may, indeed, play a major role. Our measurements by neutron diffraction on polycrystalline CaBaCo$_4$O$_7$, using the POWGEN diffractometer at Oak Ridge National Laboratory, revealed small but abrupt variations in the unit-cell parameters to be detected at T_C. As shown in Fig. 6, the variation in the cell parameter below T_C follows the variation in both the polarization and the magnetization. This suggests that the increase in the polarization below T_C is strongly linked to the magnetostriction. However, the structure of CaBaCo$_4$O$_7$ is quite complex, and the relatively large values of the estimated standard deviations on positional parameters preclude a quantitatively reliable calculation of the induced polarization. The sensitivity of the structural and electrical properties to the spin ordering is also reflected by the effect of an external magnetic field. As shown in Fig. 5(a), at 65 K (i.e., just 1 K above T_C) and for $H > 1$ T, a metamagnetic transition from a paramagnetic to a ferrimagnetic state is induced. Thus, magnetic-field application could control the change from the polar paramagnetic phase to the polar ferrimagnetic phase with a gigantic variation in the polarization.

V. CONCLUSION

This study of a CaBaCo$_4$O$_7$ single crystal demonstrates that its ferrimagnetic ordering induces a gigantic variation in its electric polarization near T_C, five times larger than the highest value reported for GdMn$_2$O$_5$.[8] Moreover, its linear magnetoelectric effect is also one of the highest that has been reported up to now.

Remarkably, this phase, which belongs to the 114 structural family, exhibits a pure tetrahedral coordination of cobalt, different from most magnoelectrics where the magnetic cations are either in octahedral or in pyramidal coordination. Several oxides of this 114 series, such as YbBaCo$_4$O$_7$,[24] TmBaCo$_4$O$_7$ (cited in Ref. 24), and YBaCo$_4$O$_7$ (Refs. 25 and 26) have been shown to exhibit, like CaBaCo$_4$O$_7$, a $k = 0$ magnetic propagation vector, which is a symmetry condition for the appearance of spontaneous magnetization and the linear magnetoelectric effect. Thus, the 114 family offers potentialities to design performing magnetoelectrics.
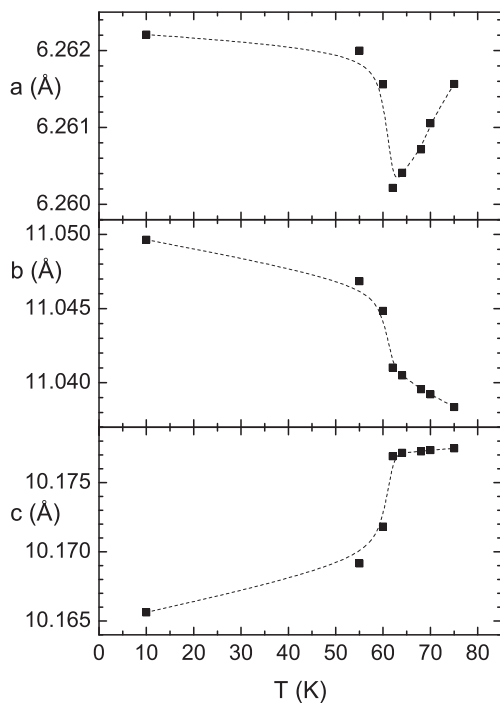
FIG. 6. From top to bottom: *a*, *b*, and *c* cell parameters of polycrystalline CaBaCo$_4$O$_7$ versus T refined from neutron-powder-diffraction data.

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[1]M. Fiebig, J. Phys. D: Appl. Phys. **38**, R123 (2005).

[2]S.-W. Cheong and M. Mostovoy, Nature Mater. **6**, 13 (2007).

[3]S. H. Chun, Y. S. Chai, Y. S. Oh, D. Jaiswal-Nagar, S. Y. Haam, I. Kim, B. Lee, D. H. Nam, K.-T. Ko, J.-H. Park, J.-H. Chung, and K. H. Kim, Phys. Rev. Lett. **104**, 037204 (2010).

[4]T. Kimura, T. Goto, H. Shintani, T. Arima, and Y. Tokura, Nature (London) **426**, 55 (2003).

[5]K. Taniguchi, N. Abe, T. Takenobu, Y. Iwasa, and T. Arima, Phys. Rev. Lett. **97**, 097203 (2006).

[6]N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, Nature (London) **429**, 392 (2004).

[7]G. Laws, A. B. Harris, T. Kimura, N. Rogado, R. J. Cava, A. Ahrarong, O. Entin-Wohlman, T. Yildrim, M. Kenzelmann, C. Broholm, and A. P. Ramirez, Phys. Rev. Lett. **95**, 087205 (2005).

[8]N. Lee, C. Vecchini, Y. J. Choi, L. C. Chapon, A. Bombardi, P. G. Radaelli, and S.-W. Cheong, Phys. Rev. Lett. **110**, 137203 (2013).

[9]R. D. Johnson, L. C. Chapon, D. D. Khalyavin, P. Manuel, P. G. Radaelli, and C. Martin, Phys. Rev. Lett. **108**, 067201 (2012).

[10]V. Caignaert, V. Pralong, A. Maignan, and B. Raveau, Solid State Commun. **149**, 453 (2009).

[11]V. Caignaert, V. Pralong, V. Hardy, C. Ritter, and B. Raveau, Phys. Rev. B **81**, 094417 (2010).

[12]K. Singh, V. Caignaert, L. C. Chapon, V. Pralong, B. Raveau, and A. Maignan, Phys. Rev. B **86**, 024410 (2012).

[13]J.-P. Rivera and H. Schmid, J. Appl. Phys. **70**, 6410 (1991).

[14]J.-P. Rivera and H. Schmid, Ferroelectrics **55**, 295 (1984).

[15]M. Clin, J.-P. Rivera, and H. Schmid, Ferroelectrics **108**, 213 (1990).

[16]M. Clin, J.-P. Rivera, and H. Schmid, Ferroelectrics **79**, 173 (1988).

[17]O. Crottaz, J.-P. Rivera, and H. Schmid, Ferroelectrics **204**, 125 (1997).

[18]J.-P. Rivera, Eur. Phys. J. B **71**, 299 (2009).

[19]N. A. Spaldin, M. Fiebig, and M. Mostovoy, J. Phys.: Condens. Matter **20**, 434203 (2008).

[20]I. Kornev, M. Bicharin, J. P. Rivera, S. Gentil, H. Schmid, A. G. M. Jansen, and P. Wyder, Phys. Rev. B **62**, 12247 (2000).

[21]E. Ascher, H. Rieder, H. Schmid, and H. Stößel, J. Appl. Phys. **37**, 1404 (1966).

[22]H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. **95**, 057205 (2005).

[23]Y. J. Choi, H. T. Yi, S. Lee, Q. Huang, V. Kiryukhin, and S.-W. Cheong, Phys. Rev. Lett. **100**, 047601 (2008).

[24]A. Huq, J. F. Mitchell, H. Zheng, L. C. Chapon, P. G. Radaelli, K. S. Knight, and P. W. Stephens, J. Solid State Chem. **179**, 1136 (2006).

[25]D. D. Khalyavin, P. Manuel, B. Ouladdiaf, A. Huq, P. W. Stephens, H. Zheng, J. F. Mitchell, and L. C. Chapon, Phys. Rev. B **83**, 094412 (2011).

[26]L. C. Chapon, P. G. Radaelli, H. Zheng, and J. F. Mitchell, Phys. Rev. B **74**, 172401 (2006).