Magnetoelectric coupling in the Haldane spin-chain system Dy_2BaNiO_5

Kiran Singh,[1,*] Tathamay Basu,[1] S. Chowki,[2] N. Mahapotra,[2] Kartik K. Iyer,[1] P. L. Paulose,[1] and E. V. Sampathkumaran[1]

[1]*Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai-400005, India*

[2]*School of Basic Sciences, Indian Institute of Technology-Bhubaneswar, Bhubaneswar, 751013, India*

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We report the results of various measurements, namely magnetization, complex dielectric permittivity, and electric polarization (P), on Dy_2BaNiO_5 as a function of temperature (T) and magnetic field (H), apart from heat capacity (C), with the primary motivation of exploring the existence of magnetoelectric (ME) coupling among Haldane spin-chain systems. The $M(T)$ and $C(T)$ data establish long-range magnetic ordering at 58 K. The most noteworthy observations are: (i) Distinct anomalies are observed in the dielectric constant (ε') vs T and loss ($\tan\delta$) vs T at different temperatures (i.e., 12.5, 30, 50, and 58 K); at low temperatures, three magnetic-field-induced transitions are observed in ε' vs H at 6, 40, and 60 kOe. These transition temperatures and critical magnetic fields track those obtained from magnetization data, establishing the existence of strong magnetoelectric coupling in this compound. (ii) Correspondingly, electric polarization could be observed as a function of T and H in the magnetically ordered state, thereby indicating magnetism-induced ferroelectricity in this compound; this result suggests that this compound is a possible multiferroic material among spin =1 (nickel-containing) compounds, with successive magnetic transitions and strong magnetoelectric coupling.

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I. INTRODUCTION

Magnetoelectric (ME) materials in which the magnetic (electric) properties can be tuned by electric (magnetic) field have gained attention because of their importance for fundamental science and technology. After the discovery of multiferroicity and ME coupling in $TbMnO_3$,[1] many new multiferroics with strong ME coupling have been discovered with different microscopic origins.[2,3] In the vast growing field of multiferroicity, many of the magnetically driven ferroelectrics are geometrically frustrated magnetic materials.

In this article, we focus our attention on the spin-chain systems of the type R_2BaNiO_5 (R = rare earths),[3–19] which do not exhibit geometrically frustrated magnetism. Among spin-chain systems, rare earth nickelates (spin, $S = 1$) have drawn interest in recent years due to observation of the Haldane gap,[20] even in the long-range magnetically ordered state[4,11,17–19] for magnetic-moment-containing rare earth members. Early on, Y_2BaNiO_5 ($S = 1$) originally was shown to exhibit the Haldane gap $\Delta_H = 10$ meV, however, without long-range ordering down to 100 mK.[5–7,9,10] The long-range magnetic ordering is missing in Y_2BaNiO_5 because the intrachain interaction is stronger than the interchain interaction. The Ni chain is isolated by Ba^{2+} and Y^{3+} (which are nonmagnetic); hence, no long-range magnetic ordering has been observed. Therefore, the observation of long-range antiferromagnetic (AFM) ordering for other members implies the significant role of R-Ni magnetic interactions.[4,12–15]

All R_2BaNiO_5 compounds crystallize in orthorhombic structure (*Immm*).[15] However, heavier rare earths (Tm, Yb, and Lu) are dimorphic, and, depending on the synthetic conditions, these can also form in the well-known *green phase*, having *Pnma* space group.[13] Compared with regular octahedra, the NiO_6 octahedra in this family is strongly distorted. The Ni-O apical distance is 1.88 Å, whereas the corresponding distance in the basal plane is 2.18 Å. Moreover, the O-Ni-O bond angle is 78°, much smaller than that for the regular octahedra.[15] Since the interchain-to-intrachain interaction ratio is very small ($\sim 10^{-2}$), one-dimensional (1D) behavior apparently is perceived to persist, even in the magnetically ordered state.[17,18] It is well-known that, for small values of $S = 1/2$ or 1, strong quantum fluctuations occur at low temperatures (T), leading to exotic ground states.[21] Therefore, the R_2BaNiO_5 series is considered to be rare, showing both classical and quantum spin dynamics in the magnetically ordered state.[18]

The magnetism of R_2BaNiO_5 compounds has been studied in detail by neutron diffraction.[15] For magnetic-moment-containing R, it is believed that there are two magnetic anomalies: one as revealed by a maximum in magnetic susceptibility (χ) vs T at a temperature, T_{max}, and another at a higher temperature (T_N) arising from three-dimensional (3D) long-range magnetic ordering. For the whole series, T_N is greater than T_{max}. In the earlier stages of investigation of this series, T_{max} was considered to be due to 3D AFM ordering;[22] subsequent neutron diffraction studies evidenced that both R^{3+} and Ni^{2+} magnetic moments actually order well above T_{max}.[4] The magnetic structure is commensurate with $k(1/2, 0, 1/2)$ in the absence of an external magnetic field (H). It may be noted that most of the compounds of this family have been known to exhibit only two magnetic-field-induced transitions below T_{max}.[12,16]

Turning to dielectric properties, recently Chen *et al.*[23] have studied the dielectric behavior of Y_2BaNiO_5. Above 80 K, this compound is not a good insulator,[6] and very high dielectric permittivity ($\varepsilon' = 10^4$ at room temperature) was observed. In the case of Ho_2BaNiO_5, linear ME coupling was reported.[24] However, to the best of our knowledge, there is no further report on the behavior of ε' vs T (except for Y_2BaNiO_5) and ε' vs H for any member of this series. As most of the R_2BaNiO_5 compounds show magnetic-field-induced transitions[12,16] and are highly insulating at low temperatures, it would be interesting to study magnetic and dielectric properties (as a function of T and H) to explore the existence of ME coupling in these systems. In this series, T_N varies with rare-earth ionic radius and maximum T_N (~65 K) is observed for R = Tb. The value of T_N for the Dy member is comparable (~58 K) to that of Tb. The Dy member is unique in this series,

as, at low T, the Ni^{2+} moment tends to align with the positive c axis (i.e., toward the Dy^{3+} magnetic moment)[15] unlike other members. In view of such interesting magnetic behavior, we have chosen this compound for the present investigation. Our results reveal that this compound behaves like a multiferroic material with strong ME coupling. Another outcome of this work is that this compound has in fact three, rather than two, magnetic-field-induced transitions.

II. EXPERIMENTAL

A polycrystalline sample of Dy_2BaNiO_5 was prepared by a standard solid-state reaction route as described in the literature.[12,15,25] The formation of the compound was ascertained by room temperature x-ray powder diffraction pattern using Cu-K_α radiation. The Rietveld refinement also confirmed phase formation, and the lattice parameters (a = 3.723(1) Å, b = 5.702(2) Å, and c = 11.208(4) Å) are in good agreement with those reported in the literature.[8,15] The dc χ measurements were carried out in the temperature interval 1.8–300 K in the presence of magnetic fields of 100 Oe and 5 kOe for zero-field-cooled (zfc) and field-cooled (fc) conditions using a commercial superconducting quantum interference device (SQUID, Quantum Design, USA) and isothermal magnetization (M) behavior was also recorded at selected temperatures with the help of a commercial vibrating sample magnetometer (VSM, Quantum Design). Additionally, heat-capacity (C) measurements were done by a relaxation method using a commercial Physical Properties Measurement System (PPMS, Quantum Design). We attempted to measure temperature-dependent dc electrical resistivity (ρ) by a four-probe method in 0 and 70 kOe magnetic fields using PPMS, as well as by a two-probe method (not shown here). The value at room temperature falls in the megaohms-cm range, and it appears to increase with decreasing temperature; below 210 K, it is found to be beyond the detection limit by four-probe measurements. Magnetoresistance was found to be negligible, as inferred from the data measured to 70 kOe. Complex dielectric permittivity was measured using an Agilent E4980A LCR meter with a home-made sample holder integrated with the PPMS. Temperature-dependent complex dielectric permittivity was measured at 30 kHz at 1V ac bias during warming (1 K min). Remnant polarization (P) as a function of T was measured with a Keithley 6517A electrometer in Coulombic mode. An electric field of 400 kV/m was applied at 70 K to align the electric dipoles and was removed after cooling to 8 K. Afterward, a capacitor was discharged for 30 min and P vs time was recorded for 5 ksec to remove stray charges, if any. P vs T was measured during warming (5 K min). For P vs H measurements, the same procedure was followed as explained for P vs T. Isothermal magnetic field dependence of dielectric behavior was measured at different temperatures (below and above T_N) at 100 kHz. The rate of change of magnetic field in all these measurements was 100 Oe/sec.

III. RESULTS

A. Magnetic susceptibility

Temperature dependence of magnetic susceptibility is shown in Fig. 1. The $\chi(T)$ behavior obtained in 5 kOe for Dy_2BaNiO_5 is presented in Fig. 1(a). The curves obtained

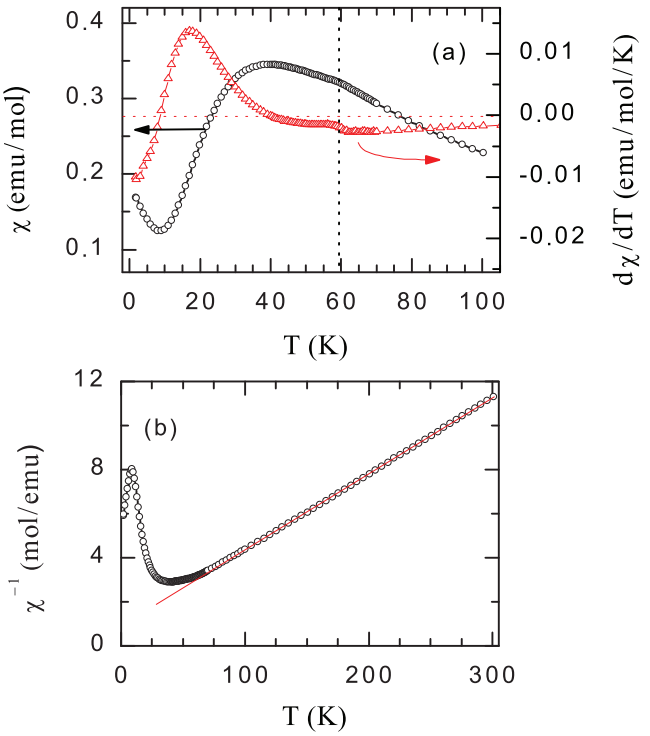

FIG. 1. (Color online) Temperature dependence of (a) zfc magnetic susceptibility (χ) measured in 5 kOe (left y axis) for Dy_2BaNiO_5, $d\chi/dT$ is plotted on right y axis; (b) Temperature dependence of inverse susceptibility; the line represents Curie-Weiss fitting in the paramagnetic region.

for zfc and fc conditions overlap; therefore, we have shown only the zfc curve. As the temperature is lowered, the plot of χ vs T shows a small kink near 58 K, which is distinctly visible in the first derivative, $d\chi/dT$ [also plotted in Fig. 1(a), right y axis], arising from the onset of long-range magnetic order. This is followed by a broad hump around 38 K, which is attributed to persistence of the 1D magnetic feature in the magnetically ordered state. Additionally, below $T \sim 10$ K, χ increases with decreasing T as though there is another magnetic transition. The inverse of χ is linear above ~100 K [Fig. 1(b)] and a Curie-Weiss fit leads to a value of -24 K for the paramagnetic Curie temperature (θ_p) and an effective magnetic moment (μ_{eff}) of the 10.73 ($\pm$0.05) μ_B/Dy atom, in agreement with the reported results.[15,26,27]

B. Heat capacity

The heat capacity of the title compound, which is of importance in inferring the onset of long-range magnetic ordering, has not been reported in the literature. We present this property in the form of C/T as a function of T in Fig. 2(a). A clear peak is observed around 58 K, attributable to 3D long-range magnetic ordering. This 3D ordering temperature is consistent with optical absorption and neutron diffraction results.[16,27] A convex-shaped feature around 18–38 K and an upturn around 10 K signal additional transitions at low temperatures. Such an additional transition at low temperature (~10 K) was also proposed by Chepurko *et al.*[16] for Er_2BaNiO_6. In order to see these features more clearly, we have shown $d(C/T)$ vs $d(T)$ in Fig. 2(b), which reveals an upturn below about 30 K

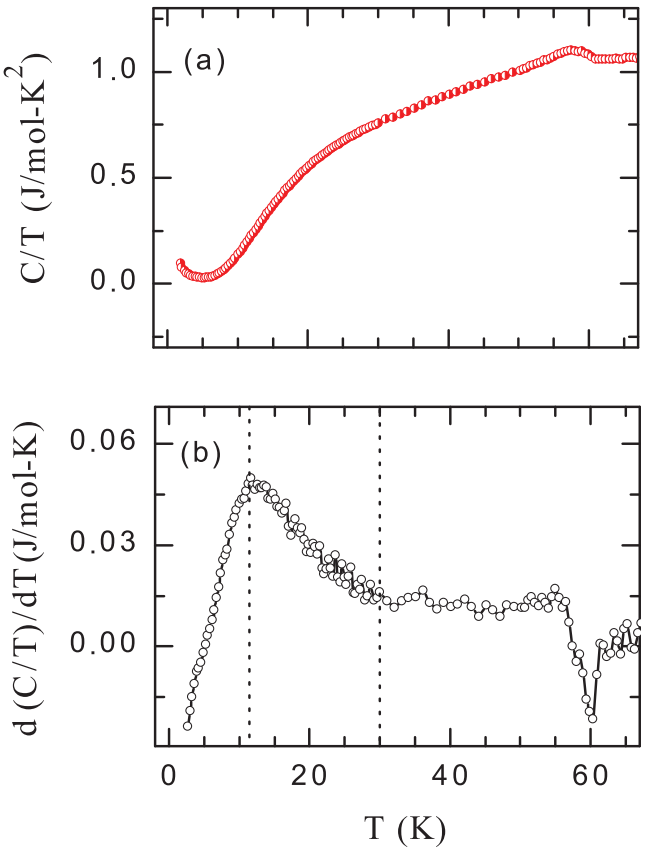

FIG. 2. (Color online) Temperature (T) dependence of (a) heat capacity (C) divided by temperature, and (b) $d(C/T)/dT$ for Dy_2BaNiO_5.

with a peak near 12 K. These features are also reflected in the $d\chi/dT$ plot [Fig. 1(a)]. We believe that such multiple features are associated with magnetism and can be related to the temperature evolution of Dy^{3+} and Ni^{2+} magnetic moments and Dy-Dy interactions.[15] Similar heat-capacity behavior has actually been observed for some other members of this rare earth series.[14,28]

C. Temperature dependence of dielectric constant and electric polarization

Figures 3(a) and 3(b) present T-dependent ε' and loss factor (tanδ) near the magnetic ordering region. The anomaly at T_N in ε' is very weak and difficult to see [Fig. 3(a)]. Although one can see a change in slope at T_N by plotting $d\varepsilon'/dT$ (not shown here), the existence of a transition can be clearly seen in the plot of $d^2\varepsilon'/dT^2$ [Fig. 3(a) inset, bottom left]. Additionally, there is a weak change in the slope around 30 K; another is also present in the range 12–15 K, as shown in the upper right inset of Fig. 3(a). The feature near 12.5 K can be seen clearly in tanδ vs T [Fig. 3(b); also see inset]. All these features can be seen clearly in the plot of $d(\tan\delta)/dT$ vs T [Fig. 3(b), right y axis], including a peak at T_N.

In order to explore the presence of ferroelectricity, remnant electric polarization was measured as a function of T. The results presented in Fig. 3(c) show that electric polarization exists in the magnetically ordered state (below T_N) indicating spin-driven polarization. Open circles represent the observed

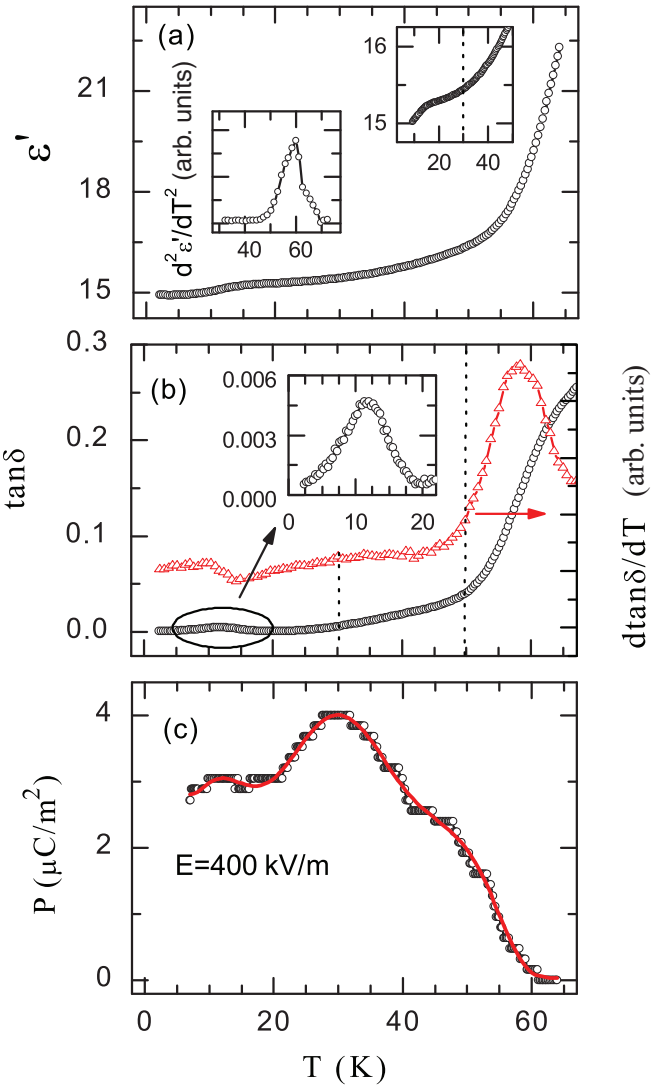

FIG. 3. (Color online) Temperature dependence of (a) the dielectric constant measured at 30 kHz, (b) tanδ (left y axis) and $d(\tan\delta)/dT$ (right y axis), and (c) the remnant polarization measured during warming for Dy_2BaNiO_5. The line through the data points in (c) represents the polynomial fit (see text for more details) as a guide to the eyes. Insets in panel (a) show $d^2\varepsilon'/dT^2$ (left, lower side) and the dielectric constant on an expanded scale (right, upper side), and the inset in panel (b) shows tanδ on expanded scales at low temperatures.

data points, and the red line is the polynomial fit (ninth order). This polynomial fit is a guide to the eyes without any other implications. Steplike features in the observed data are due to instrument resolution (1 pC), because the changes in P are very negligible for a small interval of temperature (with the data taken each second). The remnant P is less compared with that observed for Ho_2BaNiO_5.[24] In addition to the presence of polarization in the magnetically ordered state, we see distinct anomalies in other temperature ranges, viz., around 50, 38, 30, and 10 K. The feature around 50 K coincides with the temperature at which ε' and tanδ start increasing rapidly with temperature [Fig. 3(b), right y axis], and this is related to a sudden change in magnetism due to Dy. The feature around 38 K may be associated with the rotation of Ni^{3+} magnetic moments (from the negative to

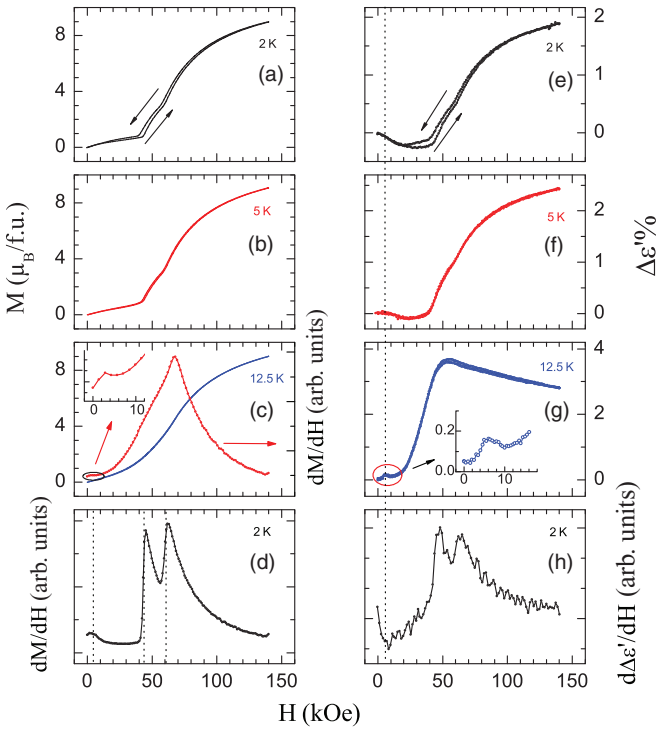

FIG. 4. (Color online) Magnetic field dependence of magnetization (a)–(c), and dielectric constant (e)–(g) for Dy_2BaNiO_5 at different temperatures. Panels (c) (right y axis) and (d) show dM/dT curves at 12.5 and 2 K, respectively. (h) $d\Delta\varepsilon'/dH$ at 2 K. Insets in panels (c) and (g) show dM/dT and the dielectric constant at 12.5 K at low magnetic fields.

the positive direction with respect to the c axis); we believe that all the temperature-induced features arise from gradual rotation of Ni magnetic moment towards the Dy moment (see below for further discussions on this aspect). In any case, observation of multiple features in similar temperature ranges in $d(\chi)/dT$, C/T, $d(C/T)/dT$, $\varepsilon'(T)$, and $P(T)$ offers direct evidence for the coupling between electric and magnetic ordering parameters.

D. Isothermal magnetoelectric coupling effects

Magnetic-field-dependent M, $\varepsilon'(T)$, and P results are presented in Fig. 4. In this figure, panels (a)–(c) show isothermal magnetization behavior at 2, 5, and 12.5 K, respectively. At low temperatures, say at 2 and 5 K, magnetic-field-induced magnetic transitions are clearly observed. The one around 45 kOe (H_{c2}) and another around 60 kOe (H_{c3}) are consistent with earlier reports.[12,16] These critical magnetic field values (H_c) correspond to the maxima in dM/dH. It is important to note that a small but clear hysteresis is observed at H_{c2} and H_{c3} which was not noticed in previous studies.[12,16] This establishes the first-order nature of these transitions. With increasing temperature, the width of the hysteresis decreases, as inferred by a comparison of the curves for 2 and 5 K. Another new observation to be noted is that, below H_{c2}, there is a small convex-shaped curvature that indicates the existence of one more magnetic anomaly [Fig. 4(a)]. We have plotted dM/dH in Fig. 4(d), which clearly reveals an additional weak feature around 6 kOe (H_{c1}). The transition at H_{c1} does not show any hysteresis. At 12.5 K [Fig. 3(c), right y axis], a clear magnetic-field-induced transition is seen in M vs H above 50 kOe, but a careful look at the derivative curve reveals the existence of more than one field-induced transition; a small but clear anomaly can be seen at a very low field [inset of Fig. 4(c)]. The magnetization value at the highest measured magnetic field at low temperatures is found to be $\sim 9\mu_B$/f.u., which agrees well with the neutron diffraction results (i.e., the sum of Dy^{3+} and Ni^{2+} ion magnetic moments at low temperature.[15] It is worth noting that magnetic-field-induced multiple transitions for 1D chain systems $Ca_3Co_2O_6$ are of interest (see, e.g., Refs. 29 and 30).

In order to explore ME coupling further, we have performed isothermal ε' vs H measurements at different temperatures up to 140 kOe and presented them in the form of $\Delta\varepsilon'$, where $\Delta\varepsilon' = [(\varepsilon'_H - \varepsilon'_{H=0})/\varepsilon'_{H=0}]$ in Figs. 4(e)–4(g) at the same temperatures as for M vs H curves (i.e., at 2, 5, and 12.5 K). Consistent with the behavior observed in M vs H data, two transitions with hysteresis are observed at 2 and 5 K near $H = 40$ and 60 kOe; it is notable that a small anomaly is seen near H_{C1} (marked with a vertical dotted line), which is clearly visible in the plot of $d\Delta\varepsilon'/dH$ for 2 K [Fig. 4(h)]. Even at 12.5 K, the low-field transition is more prominent in the $\Delta\varepsilon'$ vs H plot [Fig. 4(g)]. This shows that ε' vs H measurements are very sensitive for detecting magnetic-field-induced changes,[30,31] if there is ME coupling. Similar behavior also has been observed in the well-known multiferroic compound $CuCrO_2$,[31] in which a magnetic-field-induced transition was observed only in ε' vs H, even for single crystals. In fact, if one looks at dM/dH data carefully for Er_2BaNiO_5,[16] three magnetic-field-induced transitions can be inferred, supporting our observation. Another interesting observation is that the value of $\Delta\varepsilon'$ is quite high and is comparable to that known for $TbMnO_3$ multiferroics (along the a axis)[1] and larger than that known for other ME materials.[30,32] In fact it is also much higher than that observed for manganites.[33] Interestingly, a maximum value of $\Delta\varepsilon'$ ($\sim$4%) is observed for intermediate temperatures (e.g., at 12.5 and 15 K); then, the magnitude decreases at higher temperatures. No $\Delta\varepsilon'$ is observed above T_N (i.e., at 80 K) in the paramagnetic state.

Remnant polarization as a function of H was also measured, for instance, at 7 K. The sample was cooled with $E = 400$ kV/m from the paramagnetic/paraelectric region to 7 K, as described for P vs T measurements; then, P vs H was measured (100 Oe/sec). For a direct comparison of different order parameters (spin/charge) as a function of H, we have shown H-dependent M, ε', and P in Figs. 5(a)–5(c) at 7 K. Figure 5(c) shows that P decreases with increasing H, exhibiting a change of curvature in the vicinity of magnetic fields where there are distinct changes in other H-dependent measurements. A gigantic change in P [1500%; Fig. 5(c)] is observed with H and, at H_{c2}, even a change of sign occurs. The large change in P at the magnetic-field-induced transition is also observed for other well-known multiferroics.[1,31] Recently, a similar behavior (i.e., a large change in P and a change of P sign at the critical field) was reported in $GdMn_2O_5$.[34] All these results show one-to-one correlation with magnetic properties, which again proves the existence of ME coupling in this compound.

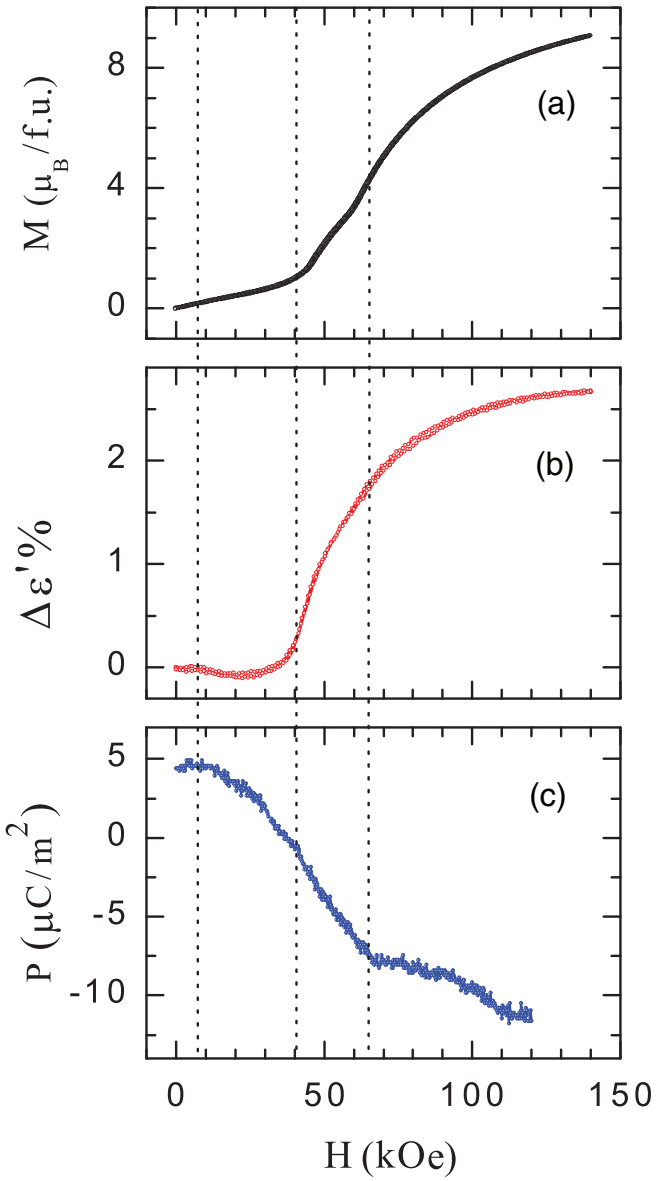

FIG. 5. (Color online) Magnetic field dependence of magnetization (a), the dielectric constant (b), and electric polarization (c) of Dy_2BaNiO_5 at 7 K.

IV. DISCUSSIONS

As mentioned above, three magnetic anomalies are observed below $T < T_{max}$, both in M vs H and ε' vs H. The presence of these magnetically induced transitions could be related to different relative orientations of Dy^{3+} and Ni^{2+} magnetic moments, based on the knowledge existing for varying temperature as elaborated below.

Ni^{2+} moments are coupled to each other antiferromagnetically along the a axis. The neutron diffraction results[15] show that, for Dy_2BaNiO_5 at low T ($T = 1.5$ K), the Ni^{2+} moments align toward the c axis (ac plane; i.e., toward the direction of Dy^{3+} moments) by making a small angle ($\theta = 17^\circ$) with the c axis. This angle of Ni moment with the c axis is very small relative to that for the rest of the members of this series.[15] The rotation of Ni^{2+} magnetic moments with decreasing temperature is strongly R-dependent, and this is due to the different anisotropy of R ions.[15,26] In the case of Dy_2BaNiO_5, at low temperatures, Ni^{2+} moments rotate toward the c axis due to the large magnetic moment of Dy^{3+} and strong $J_{Ni\text{-}Dy}$ exchange interactions.[15] Temperature evolution of Ni^{2+} moments[15] revealed that θ is different in different regions. For instance, close to T_N, it is negative with respect to the Dy^{3+} moment and fluctuating; however, with a further decrease in T, there is a crossover of θ from a negative to a positive value, and this crossover temperature is close to T_{max}. At very low T (close to 10 K), there is again a small curvature in θ [see Fig. 6(b) of Ref. 15. Moreover, this crossover of sign can also be seen clearly in the $d\chi/dT$ vs T plot [Fig. 1(a)] near 38 and 10 K.

Now, viewing all the results—M vs T, ε' *vs* T, and P vs T behavior, together with T evolution of Dy^{3+} magnetic moments and the Ni^{2+} angle with the c axis—we can infer approximately four different temperature regions: (I) $T <$ 12.5 K; (II) between 12.5 K and T_{max}; (III) from T_{max} to 50 K; and (IV) from 50 to 60 K. No structural change had been detected by neutron diffraction studies down to low temperatures;[15] only the a axis shows discontinuity at the 3D AFM ordering temperature for Tb, Ho, and Tm, indicating the presence of a magnetostriction effect as well.[8] However, no such discontinuity is known in this compound, so the magnetism is solely responsible for the appearance of polarization. The Ni^{2+} and Dy^{3+} moments are canted, and the magnetic structure is commensurate, having a single-wave vector $k(1/2, 0, 1/2)$ with the point group of the little group $2/m$.[15] On the basis of magnetic symmetry analysis, Nénert *et al.*[24] determined that the magnetic point group is $2/m'$, which is favorable for electric polarization and linear ME coupling.[35]

We can in principle extend the arguments proposed to explain the temperature-induced anomalies, in terms of the rotation of Ni moments, to the magnetic-field-induced transitions as well. As stated earlier, M vs H data at low T (2 and 5 K, region I) show a notable feature at small H ($<H_{c2}$) without any hysteresis. At H_{c2} and H_{c3}, M increases rather sharply, giving rise to hysteresis. We speculate that this sharp increase at H_{c2} and H_{c3} could be related to the Ni^{2+} moment aligning nearly toward the Dy^{3+} moment direction (c axis; i.e., Ni^{2+} and Dy^{3+} aligned ferromagnetically). Careful neutron diffraction measurements as a function of the magnetic field are urgently needed to get more precise information about the relative orientation of the Ni moment with respect to the Dy moment and to correlate with the features reported in this article. At $T \geqslant T_{max}$ (region III), we did not observe any magnetic-field-induced transitions, either in $\Delta\varepsilon'$ vs H or in M vs H.

This sample is highly insulating in the magnetic ordering temperature region. Therefore, the observed magnetoelectric coupling is the intrinsic property of this sample and does not arise from any extraneous factors, like magnetoresistance or leakage current. We would like to mention that, in order to rule out grain boundary contributions or contact effects, we have carried out impedance measurements at 50 K and obtained the Nyquist plot, that is, a plot of the real part vs the imaginary part. We found that there is no complete semicircular arc which is expected for semiconductors/relaxor materials;[36] also, we found that the plot is not sensitive to any variation of applied ac bias voltage (1 mV to 2 V), which will not be the case if the observed features arises due to external contributions.[37]

V. CONCLUSIONS

The ME coupling in Haldane spin-chain 1D nickelate Dy_2BaNiO_5 is explored by way of the T and H dependence of the dielectric constant and electric polarization. Similar to those in M vs T, anomalies are observed in ε' (tanδ) and P vs T data in the magnetically ordered state, which suggests multiferroic behavior and strong ME coupling in this compound. An additional outcome of this work is that there are three (rather than two) magnetic-field-induced transitions (say, at 2 K near ∼6, 40, and 60 kOe), with the data establishing that the dielectric data is sensitive to the detection of magnetic transitions, if there is a magnetoelectric coupling. We conclude that temperature and magnetic-field-induced transitions depend on relative orientations of Ni^{2+} and Dy^{3+} magnetic moments. Finally, the topic of successive magnetic transitions resulting in multiferroicity in $S = 1$ systems is of current interest,[38] and, in that sense, the present results provide material for further work on this topic.

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*Present address: UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India.

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