Dielectric anomalies and spiral magnetic order in $CoCr_2O_4$

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(Received 16 March 2006; revised manuscript received 25 May 2006; published 17 July 2006)

We have investigated the structural, magnetic, thermodynamic, and dielectric properties of polycrystalline $CoCr_2O_4$, an insulating spinel exhibiting both ferrimagnetic and spiral magnetic structures. Below $T_c=94$ K the sample develops long-range ferrimagnetic order, and we attribute a sharp phase transition at $T_S\approx 27$ K to the onset of long-range spiral magnetic order. Neutron measurements confirm that the structure remains cubic at 80 K and at 11 K; the magnetic ordering by 11 K is seen to be rather complex. Density functional theory supports the view of a ferrimagnetic semiconductor with magnetic interactions consistent with noncollinear ordering. Capacitance measurements on $CoCr_2O_4$ show a sharp decrease in the dielectric constant at T_S, but also an anomaly showing thermal hysteresis falling between approximately $T=50$ and 57 K. We tentatively attribute the appearance of this higher-temperature dielectric anomaly to the development of short-range spiral magnetic order, and discuss these results in the context of utilizing dielectric spectroscopy to investigate noncollinear short-range magnetic structures.

DOI: 10.1103/PhysRevB.74.024413 PACS number(s): 75.50.Gg, 75.80.+q, 75.40.Cx

I. INTRODUCTION

In recent years there has been renewed interest in investigating systems in which charge and spin degrees of freedom are strongly coupled. From colossal magnetoresistive materials[1] to diluted magnetic semiconductors,[2] studies on systems exhibiting an interplay between their magnetic and electronic properties have led to a deeper appreciation of the role of spin-charge coupling in determining the behavior of materials. The long-standing problem of understanding magnetodielectric coupling in insulating magnetic compounds has also been reconsidered lately. Recent results on magnetodielectrics have highlighted several important features in these systems, including the observation that incommensurate noncollinear magnetic structures tend to lead to large magnetocapacitive couplings, as does geometrical magnetic frustration.[3,4] With this background, it is natural to ask how one can use dielectric measurements to extract information about spiral spin structures in magnetic materials.

$CoCr_2O_4$ is a spinel ferrimagnet, with Co^{2+} ions on the *A* sites and Cr^{3+} on the *B* sites of the spinel structure. Both Co^{2+} and Cr^{3+} are magnetic; in conjunction with the fact that coupling between the *B* sites is also quite strong, a complex magnetic phase diagram emerges. Below approximately $T_c=94$ K the system has long-range ferrimagnetic order. There remain some discrepancies concerning the low-temperature magnetic phase diagram. In the original investigation on powder $CoCr_2O_4$ samples, Menyuk *et al.* found evidence for short-range spiral magnetic order below $T\sim 86$ K, and long-range spiral magnetic order below $T\sim 31$ K.[5] Motivated by suggestions that ferrimagnetic spiral long-range order in $CoCr_2O_4$ should be unstable, Tomiyasu *et al.* investigated both $CoCr_2O_4$, and $MnCr_2O_4$ through neutron and magnetization measurements on single crystals.[6] These more recent studies suggest that the spiral component develops incommensurate short-range order below approximately $T=50$ K, and that this short-range order persists to the lowest temperatures with a correlation length of only 3.1 nm at $T=8$ K. The authors attribute this behavior to weak geometric magnetic frustration prevalent in the spinel structure.

These properties suggest that $CoCr_2O_4$ would be a promising material for investigations on magnetodielectric coupling in systems with noncollinear magnetic order. $CoCr_2O_4$ is insulating, and has two different types of magnetic structures (ferrimagnetic and spiral). Measuring the dielectric constant in phases with both the ferrimagnetic and spiral components will offer insight into how dielectric properties couple to different magnetic structures within the same material.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

Ceramic samples (beautiful jade-green pellets) were prepared from cobalt oxalate $[Co(C_2O_4)_2\cdot 2H_2O]$ and chromium oxide (Cr_2O_3) by heating well-ground mixtures initially at 800 °C for close to 24 h followed by regrinding, pelletizing, and heating at 1000 °C for 24 h. The samples were initially characterized by laboratory powder x-ray diffraction (Scintag X-II, Cu $K\alpha$ radiation) and then by time-of-flight powder neutron diffraction at room temperatures, 80 and 11 K at the neutron powder diffractometer[7] at the Lujan Center at Los Alamos National Laboratory. For the measurements, the samples were contained in vanadium cans.

Calculations were performed using the projector augmented wave[8] method implemented in the Vienna *ab-initio* simulation package (VASP).[9] The cubic spinel structure (space group $Fd\bar{3}m$) with the lattice parameters fixed to the experi-

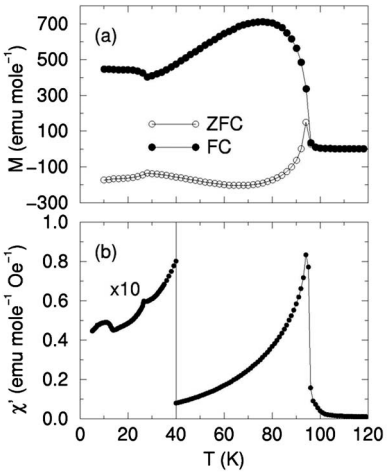

FIG. 1. (a) Zero-field-cooled (ZFC) and field-cooled (FC) dc magnetization of $CoCr_2O_4$ measured in an applied field of $H=100$ Oe. (b) Real part of the ac susceptibility of $CoCr_2O_4$ measured at $\omega/2\pi=10$ kHz. Data below 40 K have been shown in an expanded view.

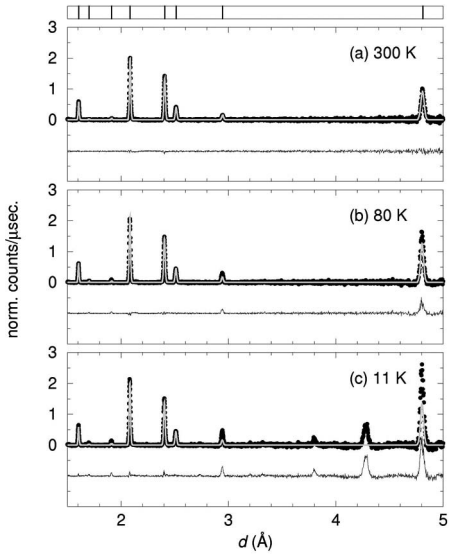

FIG. 2. Time-of-flight neutron powder diffraction at (a) 200, (b) 80, and (c) 11 K. The symbols in each panel are data, the lines are fits using the Rietveld method to the nuclear structure, and the traces at the bottom of each panel are the difference profiles. The peaks in the difference profiles that emerge as the temperature is lowered arise from long-range magnetic ordering. Vertical lines at the top of the plot are expected positions of nuclear reflections. Crystal structure data: space group $Fd\bar{3}m$, $a=8.3294(1)$ Å at 300 K, 8.3224(1) Å at 80 K, and 8.3211(1) Å at 11 K. Co at (1/8,1/8,1/8), Cr at (1/2,1/2,1/2), and O at (x,x,x) with $x=0.2617(1)$ at all three temperatures.

mentally obtained $a=8.3351$ Å was used, with an internal structural parameter for the oxygen of $x=0.264$ determined from the diffraction data. Different collinear magnetic structures were calculated in order to extract the Heisenberg exchange constants. The plane wave energy cutoff was 400 eV and we used an $8\times8\times8$ Monkhorst-Pack mesh of k points. The local density approximation (LDA) $+U$ method of Dudarev *et al.*[10] was used and U_{eff} was varied independently on both the Co and Cr sites.

We measured the temperature and field dependence of the dc magnetization of $CoCr_2O_4$ using a Quantum Design MPMS superconducting quantum interference device magnetometer, operating between $T=5$ and 350 K, and measured the ac magnetization of the sample on a Quantum Design physical property measurement system (PPMS) at frequencies between $\omega/2\pi=100$ and 10 kHz. We measured the specific heat of $CoCr_2O_4$ as a function of temperature with a quasiadiabatic method on the PPMS using a 20 mg pressed powder pellet. In order to measure the dielectric constant, we pressed approximately 75 mg of $CoCr_2O_4$ into a $5\times5\times1.5$ mm^3 pellet, and fashioned electrodes on opposite faces of the pellet using conducting silver epoxy. We measured the dielectric constant between $\omega/2\pi=1$ kHz and 1 MHz with an Agilent 4284A *LCR* meter, using the PPMS for temperature and magnetic field control. The data at lower frequencies were qualitatively similar to the higher-frequency measurements, although they were somewhat noisier and displayed larger losses, possibly due to conduction at the grain boundaries. All dielectric data presented were measured at 30 kHz.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the magnetization as a function of temperature measured in a 100 Oe field on warming after cooling in zero field (ZFC), and while cooling in a 100 Oe field (FC). The FC data are qualitatively similar to the data obtained by Tomiyasu *et al.*[6] on single crystals but the ZFC data show a negative magnetization at low temperatures. We attribute this to the presence of uncompensated spins at grain boundaries of our polycrystalline samples. The magnetization shows a large increase below the onset of ferrimagnetic long-range order at $T_c=95$ K, and there is an anomaly at $T_S=27$ K associated with spiral magnetic order in the system. It should be noted that the anomaly at $T_S=27$ K is sharper than that presented in the Tomiyasu *et al.* data.[6]

Figure 1(b) shows the real part of the ac susceptibility of $CoCr_2O_4$ acquired at a frequency of 10 kHz. A very large peak in χ' is observed at T_c. The magnified trace at low temperatures shows that there is also an anomaly at χ' at $T_S=27$ K, consistent with the sharp anomaly in the dc magnetization measurements. Furthermore, there is another clear magnetic feature at approximately $T=13$ K, which is more difficult to observe in the dc measurements. Tomiyasu *et al.* associate this feature with a saturation of the correlation length for the spiral component on cooling.[6] These bulk magnetization measurements conclusively show the existence of magnetic features at $T_c=95$ K and $T_S=27$ K, associated with the ferrimagnetic and spiral magnetic structures, respectively, and a third magnetic feature at $T=13$ K.

In order to get more information about the magnetic transitions in $CoCr_2O_4$, we also conducted neutron measurements on these samples, which at this stage, can only be considered preliminary. Figure 2 displays the bank of time-of-flight neutron scattering data with largest d spacings from $CoCr_2O_4$ powders. The Rietveld fits[11] to the nuclear structure

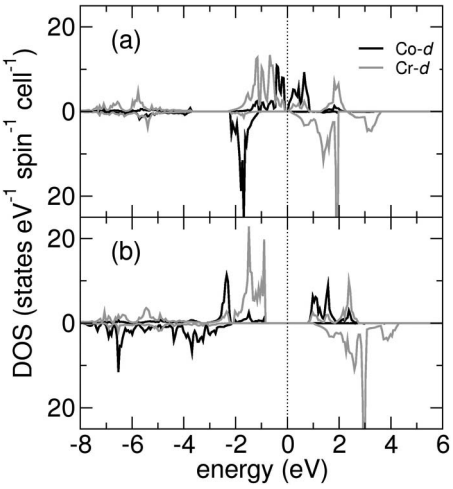

FIG. 3. Partial densities of Co d and Cr d states obtained for (a) $U_{\mathrm{eff}}^{\mathrm{Co}}=U_{\mathrm{eff}}^{\mathrm{Cr}}=0$ eV (LSDA) and (b) $U_{\mathrm{eff}}^{\mathrm{Co}}=4$ eV and $U_{\mathrm{eff}}^{\mathrm{Cr}}=2$ eV. Collinear Néel-type magnetic ordering was assumed.

at the three temperatures are also shown. At 300 K, the data are completely fitted to the nuclear structure of this spinel compound. At 80 K, below the first collinear magnetic ordering temperature, we find that some of the peaks whose nuclear contribution are fitted have a residual intensity seen clearly in the difference spectra. This is characteristic of collinear magnetic ordering, since new peaks are not observed. At 11 K, the data reveal that the intensities of a number of peaks are not correctly fitted, as well as new reflections which have come about because of the long-range noncollinear magnetic order, again evident in the difference spectrum. While we have not at this stage been able to completely establish the magnetic structure, we present these data to strengthen our interpretation of the magnetic and transport measurements. No change in the nuclear structure is observed from the three data sets, and the spinel cell parameter changes only very little from 80 K where $a=8.3224(1)$ Å to 11 K where $a=8.3211(1)$ Å.

The electronic structure of $CoCr_2O_4$ was calculated using the LSDA+U methodology. Figure 3 displays the total density of states and the partial densities of Co d and Cr d states obtained using $U_{\mathrm{eff}}^{\mathrm{Co}}=U_{\mathrm{eff}}^{\mathrm{Cr}}=0$ eV (LSDA, top panel), as well as $U_{\mathrm{eff}}^{\mathrm{Co}}=4$ eV and $U_{\mathrm{eff}}^{\mathrm{Cr}}=2$ eV (lower panel) and a collinear Néel-type magnetic structure (Co spins antiparallel to Cr spins). The system is an insulating fully spin-polarized ferrimagnetic semiconductor already in the LSDA, albeit with a very small gap, less than 0.1 eV. Application of U on either of the two magnetic sites enlarges the gap but only application of U on both sites leads to a significant gap of greater than 1 eV. The calculations show that this system can be expected to be a robust insulator and therefore promising for magnetodielectric measurements.

We also extracted the Heisenberg exchange coupling constants by calculating the total energy differences for different collinear magnetic configurations. It has been shown by Kaplan[12] that using a simple Heisenberg model for the cubic spinel structure with only nearest-neighbor couplings J_{AB} and J_{BB}, the magnetic ground-state structure is determined by the parameter $u=(4J_{BB}S_B)/(3J_{AB}S_A)$, where S_A and S_B denote the

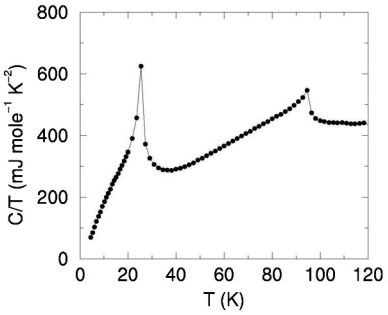

FIG. 4. Specific heat measurements on $CoCr_2O_4$ at $H=0$, plotted as C/T vs T.

spins of the A- and B-site cations, respectively. The collinear ferrimagnetic Néel state is the stable ground state for $u<u_0=8/9$, whereas for larger values of u noncollinear spiral ordering is expected. The Heisenberg exchange constants, extracted from our calculations using the reasonable values $U_{\mathrm{eff}}^{\mathrm{Co}}=4$ eV and $U_{\mathrm{eff}}^{\mathrm{Cr}}=2$ eV, are $S_AJ_{AB}S_B=5.0$ meV, $S_BJ_{BB}S_B=2.4$ meV, and $u=0.65$. Increasing $U_{\mathrm{eff}}^{\mathrm{Co}}$ and decreasing $U_{\mathrm{eff}}^{\mathrm{Cr}}$ leads to a larger value of u, eventually exceeding the critical value $u_0=8/9$. In addition, we also extracted the coupling constant J_{AA} which is neglected in the treatment of Kaplan. For the same values of U as above ($U_{\mathrm{eff}}^{\mathrm{Co}}=4$ eV and $U_{\mathrm{eff}}^{\mathrm{Cr}}=2$ eV) we obtain $S_AJ_{AA}S_A=0.7$ meV. This value is not necessarily negligible and indicates that the coupling between the A-site cations could play an important role in the magnetic properties of cubic spinels and in fact lead to noncollinear magnetic order even for values of u smaller than $u_0=8/9$. The possible importance of A-site coupling has also been pointed out in a recent experimental study of the spinel systems MAl_2O_4 (M=Co,Fe,Mn).[13] A detailed analysis of the U dependence of the electronic structure and magnetic couplings in $CoCr_2O_4$ is in progress. From the results presented in this work it can be concluded that the calculated values of the exchange coupling constants are consistent with the appearance of noncollinear magnetic order and that in addition, A-site coupling, a factor that is usually ignored, might be important in understanding the magnetic properties of this system.

In an attempt to establish whether the spiral magnetic transition at $T_S=27$ K is long range[5] or short range,[6] we measured the specific heat of our polycrystalline $CoCr_2O_4$ sample on warming from base temperature. The thermodynamic data presented in Fig. 4, including both the lattice and magnetic contributions to heat capacity, strongly suggest that there are two transitions to magnetic states with long-range order, one occurring at $T_c=94$ K and the second at $T_S=27$ K. Specifically, the sharp peak in C/T at $T_S=27$ K is indicative of long-range collective ordering. The development of long-range order in a polycrystalline sample which is absent in single-crystal samples[6] is unusual, but has also been observed in $FeCr_2S_4$.[14] We can approximate the entropy under the peaks in Fig. 4 to estimate the degree of spin ordering in the long-range order at each transition. The entropy lost by $CoCr_2O_4$ at T_c is approximately 1 J/K per mole, while the entropy change at $T_S=27$ K is approximately 1.5 J/K per mole, both at $H=0$. These changes in entropy

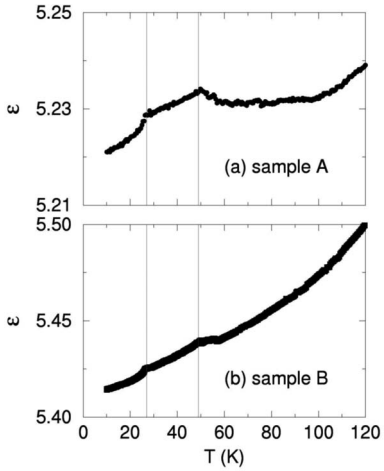

FIG. 5. (a) Dielectric constant of $CoCr_2O_4$ sample *A* measured at $H=0$ as a function of temperature. (b) Dielectric constant of $CoCr_2O_4$ sample *B* measured at $H=0$ as a function of temperature. Vertical lines are drawn at 27 and 49 K to help locate the dielectric anomalies. All data were acquired at $\omega/2\pi=30$ kHz.

are small compared to the expected change in entropy for fully spin-ordered $CoCr_2O_4$ of 34.6 J/K per mole (using the spin-only values for Co^{2+} and Cr^{3+}), suggesting that these transitions involve a rearrangement of clusters of spins. This picture is consistent with the relatively large specific heat exhibited by $CoCr_2Co_4$ over the entire temperature range shown, which demonstrates that significant short-range magnetic order is likely developing over a wide range of temperatures. We do not see any features in the specific heat which could be associated with a thermodynamic transition occurring at $T=13$ K.

One of the primary motivations for these experiments was to investigate what effect the ferrimagnetic and spiral magnetic transitions would have on the dielectric constant of $CoCr_2O_4$. These data are plotted in Figs. 5(a) and 5(b) which show the dependence of the dielectric constant on temperature for two different polycrystalline $CoCr_2O_4$ samples measured on warming. In both these samples, the dielectric constant depends only weakly on temperature, with sample *B* showing a variation of approximately 1% over the entire temperature range, and sample *A* showing an even smaller change. Differences in the magnitude of the dielectric constant can be attributed to errors in determining the geometrical capacitance factor. Differences in the temperature dependence may possibly arise from small differences in conductivity between the two samples. Both samples were structurally identical (verified by powder x-ray diffraction) but sample *B* was better sintered.

The general features in the dielectric constant are very similar for both these samples. Most notably, there is a well-defined drop in dielectric constant coincident with the onset of long-range spiral magnetic order at $T_S=27$ K (indicated with a vertical line). This sharp decrease is a signature of the coupling between the dielectric properties and magnetic structure, and shows no dependence on measuring frequency (not plotted). The change in dielectric constant is fairly small, only 0.2% between $T_S=27$ K and the base temperature. This should be compared with $EuTiO_3$ (Ref. 15) and $SeCuO_3$ (Ref. 16) which show larger changes on ordering (3.5% and 2%, respectively). The small magnitude of the shift in the dielectric constant of $CoCr_2O_4$ is consistent with the idea that a small number of spin clusters order at T_S, as evidenced by the thermodynamic data discussed previously. We mention that the very small change in lattice parameter between 80 and 11 K observed in neutron scattering data (less than 0.02%) preclude the shift from simply reflecting magnetoelastic effects.

There is no clear dielectric feature at the ferrimagnetic ordering temperature T_c. There may be a subtle change of slope observable in sample *A*, but this is not seen in sample *B*, which shows much larger intrinsic dependence of the dielectric constant on temperature. The lack of a sharp anomaly at T_c suggests that there is at best only weak coupling between the dielectric constant of $CoCr_2O_4$ and the ferrimagnetic component of the magnetic structure. Furthermore, there is no dielectric feature associated with the $T=13$ K transition. Since this magnetic feature is believed to be related to the spiral magnetization component,[6] one would expect to see a clear anomaly at 13 K. However, specific heat measurements show that only a small number of spins (or spin clusters) are likely to be involved in this transition, which perhaps explains the absence of any dielectric feature.

The dielectric constant of $CoCr_2O_4$ couples only to the spiral spin structure, and not to the ferrimagnetic structure. The shift in dielectric constant observed in many magnetodielectric materials is believed to arise from strong spin-phonon coupling.[15,16] Within this framework, the phonon mode giving rise to this magnetodielectric behavior must not couple to magnetic order along the (001) direction, but should be sensitive to spiral spin ordering with a propagation vector along the $Q=(\delta,\delta,0)$ direction in the (001) plane.[6] This observation provides an important symmetry restriction on allowed forms for the spin-lattice coupling in $CoCr_2O_4$. It is known that noncollinear spin structures can break spatial inversion symmetry to obtain magnetically induced ferroelectric order in magnetoelectric multiferroics;[17,18] it is likely that breaking a spatial symmetry could also affect dielectric properties. Further investigations on the microscopic mechanisms for spin-phonon coupling in $CoCr_2O_4$ will rely on a detailed understanding of the phonon modes in this system.

We find evidence for one further temperature-dependent dielectric anomaly in $CoCr_2O_4$. The dielectric constant shows a distinct peak at approximately $T=50$ K for the two samples (indicated by a vertical line in Fig. 5). More precisely, measurements on sample *B* seem to indicate the presence of a series of peaks, while sample *A* rather exhibits one broader peak. The magnitude of the increase in dielectric constant at this temperature is comparable to the decrease in dielectric constant below $T_S=27$ K. However, the origins of this feature are less clear. Neither the magnetization data in Fig. 1 nor the specific heat data in Fig. 5 show any evidence for a phase transition at this temperature. Additionally, this anomaly has a rather broad onset, which varies somewhat with sample history. Since $CoCr_2O_4$ does not have any structural phase transitions at low temperatures, this anomaly must have a magnetic origin. Specifically, we believe that this dielectric anomaly arises from the onset of short-range

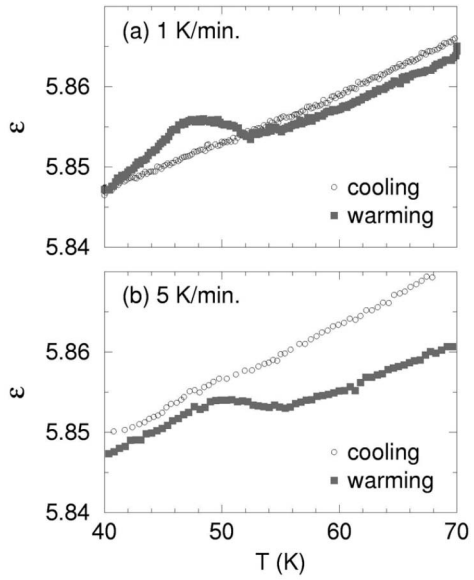

FIG. 6. (a) Dielectric constant of $CoCr_2O_4$ near $T=50$ K measured on cooling and warming at 1 K/min. (b) Dielectric constant of $CoCr_2O_4$ near $T=50$ K measured on cooling and warming at 5 K/min. All data were acquired at $\omega/2\pi=30$ kHz.

spiral magnetic order, which has also been shown to occur at approximately $T=50$ K.[6]

As a further probe of this anomaly, we measured the dielectric constant on warming and cooling at different rates. At the fastest rate of 5 K/min, there is a shift of approximately 1 K in T_S on warming and cooling, suggesting that there may be some small thermal decoupling. There is no such decoupling observed at a warming/cooling rate of 1 K/min. Figure 6 plots the dielectric constant of $CoCr_2O_4$ measuring on warming and cooling at 1 [Fig. 6(a)] and 5 K/min [Fig. 6(b)]. In both cases, there is *no* anomaly when the dielectric constant is measured on cooling, but there is a clear feature in the dielectric constant when the sample is warmed. This thermal hysteresis may arise from a nonequilibrium distribution of regions of short-range spiral magnetic order. Furthermore, the peak temperature for this anomaly occurs at a higher temperature ($T=50$ K) when the sample is warmed at 5 K/min as compared to when it is warmed at 1 K/min ($T=48$ K), although the thermal decoupling at 5 K/min makes a quantitative comparison difficult. Below $T_S=27$ K $CoCr_2O_4$ develops long-range spiral order. On warming, the disappearance of a nonequilibrium distribution of spiral magnetic clusters may be responsible for the dielectric signal at $T=50$ K. Conversely, when the sample is cooled from higher temperatures, there would be no spiral magnetic clusters present, and therefore no shift in the dielectric constant.

In summary, we have presented extensive magnetic, thermodynamic, neutron, and dielectric data on $CoCr_2O_4$. These results are consistent with a phase transition to a ferrimagnetically ordered state at $T=94$ K and we have conclusive evidence for a second transition to a phase with long-range spiral magnetic order below $T_S=27$ K in our polycrystalline sample. Magnetocapacitive measurements show that the dielectric constant of $CoCr_2O_4$ couples to the spiral magnetic order parameter, but is insensitive to the ferrimagnetic spin component. This limits the allowed spin-phonon coupling symmetry in this system, and places restrictions on the possible microscopic mechanism for the observed magnetodielectric shifts. Understanding magnetodielectric coupling in $CoCr_2O_4$ may help illuminate the mechanisms for magnetically induced ferroelectric order in magnetoelectric multiferroics, where noncollinear spin structure is known to be an important ingredient for spin-charge coupling.[18] The dielectric constant of $CoCr_2O_4$ is also found to be affected by the development of short-range spiral magnetic order. This suggests that in materials with strong spin-phonon coupling, it may be possible to use capacitive measurements to probe short-range magnetic correlations. Very recent measurements suggest that $CoCr_2O_4$ is multiferroic,[19] highlighting the importance of understanding the origins of spin-charge coupling in this system.

Note added in proof. Recent measurements on single crystal $CoCr_2O_4$ show a peak in the heat capacity at T_S,[19] consistent with long-range spiral magnetic order in these samples.

ACKNOWLEDGMENTS

The work at UCSB was supported by the National Science Foundation through the MRL program (Grant No. DMR05-20414), and through a Chemical Bonding Center Grant No. CHE04-34567. Measurements at the Lujan Center at Los Alamos Neutron Science Center were supported by the Department of Energy Office of Basic Energy Sciences and Los Alamos National Laboratory funded by Department of Energy under Contract No. W-7405-ENG-36. M.A.H. thanks the Royal Society and K.P. thanks the NSF for funding.

[1] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science **264**, 413 (1994).
[2] H. Ohno, Science **281**, 951 (1998).
[3] T. Goto, T. Kimura, G. Lawes, A. P. Ramirez, and Y. Tokura, Phys. Rev. Lett. **92**, 257201 (2004).
[4] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature (London) **426**, 55 (2003).
[5] N. Menyuk, K. Dwight, and A. Wold, J. Phys. (Paris) **25**, 528 (1964).
[6] K. Tomiyasu, J. Fukunaga, and H. Suzuki, Phys. Rev. B **70**, 214434 (2004).
[7] Th. Proffen, T. Egami, S. J. L. Billinge, A. K. Cheetham, D. Louca, and J. B. Parise, Appl. Phys. A: Mater. Sci. Process. **74**, 163 (2002).

[8] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[9] Computer code VASP, http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html
[10] S. L. Dudarev, G. A. Botton, S. A. Savrasov, Z. Szotek, W. M. Temmerman, and A. P. Sutton, Phys. Status Solidi A **166**, 429 (1998).
[11] A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report No. LAUR 86-748, 2000 (unpublished); B. H. Toby, J. Appl. Crystallogr. **34**, 210 (2001).
[12] T. A. Kaplan, Phys. Rev. **119**, 1460 (1960).
[13] N. Tristan, J. Hemberger, A. Krimmel, H.-A. Krug von Nidda, V. Tsurkan, and A. Loidl, Phys. Rev. B **72**, 174404 (2005).
[14] R. Fichtl, V. Tsurkan, P. Lunkenheimer, J. Hemberger, V. Fritsch, H.-A. Krug von Nidda, E.-W. Scheidt, and A. Loidl, Phys. Rev. Lett. **94**, 027601 (2005).
[15] T. Katsufuji and H. Takagi, Phys. Rev. B **64**, 054415 (2001).
[16] G. Lawes, A. P. Ramirez, C. M. Varma, and M. A. Subramanian, Phys. Rev. Lett. **91**, 257208 (2003).
[17] G. Lawes, A. B. Harris, T. Kimura, N. Rogado, R. J. Cava, A. Aharony, O. Entin-Wohlman, T. Yildirim, M. Kenzelmann, C. Broholm, and A. P. Ramirez, Phys. Rev. Lett. **95**, 087205 (2005).
[18] M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).
[19] Y. Yamasaki, S. Miyasaka, Y. Kaneko, J.-P. He, T. Arima, and Y. Tokura, Phys. Rev. Lett. **96**, 207204 (2006).