Composition dependence of the anomalous Hall effect in $Ca_xSr_{1-x}RuO_3$ films

P. Khalifah
Department of Chemistry, University of Massachusetts-Amherst, Amherst, Massachusetts 01003, USA
and MSTD Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

I. Ohkubo
Department of Applied Chemistry, The University of Tokyo, Bunkyo-Ku, Tokyo 113-8656, USA
and MSTD Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

B. C. Sales, H. M. Christen, and D. Mandrus
MSTD Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

J. Cerne
Department of Physics, University at Buffalo, SUNY, Buffalo, New York 14260, USA
(Received 12 September 2006; revised manuscript received 20 April 2007; published 3 August 2007)

A series of 12 epitaxial films was grown across the entire range of the solid solution $Ca_xSr_{1-x}RuO_3$ in order to systematically examine the behavior of the anomalous Hall effect in this system. While all samples in this series are known from bulk studies to behave as Curie-Weiss paramagnets at high temperatures, samples with less than 70% Ca also order ferromagnetically with a maximal Curie temperature (T_C) of ~160 K for pure $SrRuO_3$. Temperature (T) and magnetic field (H) dependent transport measurements were used in tandem with mean field simulations of sample magnetization (M) to track the composition and temperature dependence of the ordinary (R_o) and anomalous (R_s) parts of the Hall resistivity (ρ_H) in this system using the standard relation $\rho_H = R_oB + R_s 4\pi M$. In the high-temperature Curie-Weiss paramagnetic regime, the only temperature dependence of the Hall resistivity comes from the anomalous portion, allowing the ordinary and anomalous contributions to ρ_H to be estimated via Curie-Weiss type fits. R_s was observed to be positive and nearly T independent at high temperatures (>200 K) and smoothly increased with increasing Ca content in this regime. In all ferromagnetic samples, R_s decreased significantly on cooling below T_C in response to magnetic ordering, actually changing sign for samples with ≤20% Ca. This behavior is consistent with a two-component behavior of R_s, with the two different regimes (above T_C and below T_C) resulting from substantial changes in the band structure of this itinerant ferromagnet on crossing T_C. The symmetric behavior of the anomalous Hall effect around the ferromagnetic → paramagnetic quantum phase transition is perhaps an indicator of hidden magnetic order in $CaRuO_3$.

DOI: 10.1103/PhysRevB.76.054404 PACS number(s): 72.20.My, 72.80.Ga, 73.50.−h

I. INTRODUCTION

Although the Hall coefficient is generally considered a measure of carrier concentration, it has been known since the early experiments of Hall more than a century ago[1] that there can be a second "anomalous" component of the Hall response which is related to sample magnetization. The Hall resistivity in such samples is described by the formula $\rho_H = R_oB + R_s 4\pi M$, where the coefficient of "ordinary" contribution (R_o) is related to the carrier concentration via the relation $R_o = -1/ne$. There is no such expression for the coefficient describing the anomalous contribution (R_s), and a definitive understanding of this coefficient has eluded physicists for the last 100 years. R_s is often described as potentially having an extrinsic and an intrinsic component, which, respectively, have a linear and quadratic dependence on the sample resistivity (ρ_{xx}). The total Hall resistivity can therefore be described as $\rho_H = R_oB + (a\rho_{xx} + b\rho_{xx}^2)4\pi M$. The combined quantity $4\pi Mb$ is also sometimes referred to as σ_{xy}^{AHE}, as it has units of Ω^{-1} cm^{-1} and corresponds to the intrinsic Hall conductivity of the material.[2] If ρ_{xx} has an appreciable temperature dependence, the extrinsic and intrinsic contributions can often be determined.[3]

In most magnetic systems, it is impossible to accurately measure the ordinary Hall effect (OHE) without first separating out the anomalous Hall effect (AHE). In the absence of a good measure of the AHE in magnetic systems, large errors in determining the carrier concentration and even in assigning the sign of the carriers are possible. This is certainly the case for $SrRuO_3$, whose primary carriers have previously been identified as electrons,[4] holes,[5] or changing as a function of temperature.[6,7]

Recent work ascribing the origin of the anomalous Hall effect to Berry's phase effects within the band structure of compounds has shown great promise in quantitatively describing the behavior of a handful of ferromagnetically ordered (FM) systems, with calculations of σ_{xy}^{AHE} closely matching experimental results.[8,9] However, the anomalous Hall effect is potentially present in all systems with a local magnetic moment and not just in ferromagnets. This work explores the anomalous Hall effect both inside and outside of the FM regime. By continuously doping the $Ca_xSr_{1-x}RuO_3$ system from ferromagnetic $SrRuO_3$ to paramagnetic $CaRuO_3$, the response of R_s to a changing Fermi surface can be investigated as the quantum phase transition at 70% Ca is crossed.[10] The $Ca_xSr_{1-x}RuO_3$ system is of particular interest since the two end members, $SrRuO_3$ and $CaRuO_3$, are known

to have an unusual temperature-induced sign change in their Hall resistivity.[6] Data obtained from tunable magnetic systems will be crucial in evaluating the ability of theoretical models to describe real materials and will answer some open questions on the sensitivity of the anomalous Hall effect to small Fermi surface changes.

II. EXPERIMENT

Thin films samples of the $Ca_xSr_{1-x}RuO_3$ series were prepared using a custom-built multitarget pulsed laser deposition system.[11] Desired $Ca_xSr_{1-x}RuO_3$ stoichiometries were prepared by varying the ratio of pulses on commercially obtained (Praxair) $CaRuO_3$ and $SrRuO_3$ targets. Films were grown with a KrF excimer laser (248 nm), which had an energy density of 3.87 J/cm^2. The lanthanum aluminum oxide substrate temperature was maintained at 675 °C under an oxygen pressure of 80 mTorr. Compositions were verified using elemental dispersive x-ray analysis and Rutherford backscattering techniques. Film thicknesses were determined by edge analysis on a scanning electron microscope.

The electrical resistivity (ρ_{xx}) and Hall resistivity (ρ_H or ρ_{yx}) of the samples were measured in the horizontal rotational stage of a physical property measurement system (PPMS) (Quantum Design). In order to allow sequential measurement of ρ_{xx} and ρ_H at each set of conditions, a total of six contacts (two shared current terminals and four voltage terminals) were painted on each bar-shaped sample using silver epoxy (Epotek, H20B). A low-temperature air anneal (at least 1 h at 300 °C) was used to minimize contact resistance. The 1 mA current used for measurements did not cause sample heating under the measurement conditions (5–350 K). Due to the demagnetization factors of the thin films, it was assumed that $B=\mu_0 H$ during the measurement and analysis of samples.

Misalignments of the Hall terminals were corrected for by taking the difference between the measured Hall voltages at applied fields of $+H$ and $-H$ and normalizing the readings. For the measurements of ρ_H during temperature sweeps, a constant field strength (9 T) and orientation ($+H$) were maintained, and a negative field at the sample surface was obtained by flipping the sample by 180°. For ferromagnetic samples with magnetic hysteresis at low applied fields, there is more than one way that ρ_H can be defined, due to the fact that the sample magnetization at a given field within the hysteretic region will differ depending on whether the field is being ramped up or down $[M_\uparrow(H) \neq M_\downarrow(H)]$. Thus, the two sensible methods of defining the Hall resistivity as a function of the Hall voltage V, applied current I, and sample thickness t at a given applied field H measured while the applied field is being increased ($\uparrow$) are either the "even sweep" manner, where $\rho_{H\uparrow}(H)=\frac{t}{I}\frac{1}{2}[V_\uparrow(H)-V_\uparrow(-H)]$, or the "odd sweep" fashion, where $\rho_{H\uparrow}(H)=\frac{t}{I}\frac{1}{2}[V_\uparrow(H)-V_\downarrow(-H)]$. We believe that odd sweep method is most appropriate for ferromagnets as the even sweep method artificially forces ρ_H to be zero at $H=0$ in a magnetized sample, despite the finite Hall voltages from the anomalous Hall effect present in such a sample. One important consequence of the odd sweep method is that ρ_H(H) will exhibit different values for the different directions of the field sweep $[\rho_{H\uparrow}(H) \neq \rho_{H\downarrow}(H)]$, allowing the hysteresis of ρ_H to be properly visualized.

Thin film Seebeck coefficients were obtained using the thermal transport platform of a Quantum Design PPMS. Thermal leads (15 mil Cu wire) were attached with silver epoxy to the $LaAlO_3$ substrate. Voltage readings were obtained by using separate 1 mil Pt wires to connect the central thermal leads to the film surface, again using silver epoxy.

Mean field theory was used to model the H, T, and composition dependence of the thin film magnetization $M(H,T,x)$ of the $Ca_xSr_{1-x}RuO_3$ system using a simple Brillouin function.[12] The two sample-dependent parameters were the spin interaction strength λ and the saturation magnetization M_{sat}. A linear fit ($\theta=152-233x$) to the literature Curie-Weiss θ values of Kanbayashi[13] was used as a starting estimate for λ through the derived relation $\lambda=\theta/C$. This suffices to model both the ferromagnetic (⩽70% Ca) and paramagnetic (⩾75% Ca) samples, dealing reasonably with both positive and negative θ values. The free magnetic moment (represented by C) used inside the Brillouin function was fixed at 2 μ_B, while the saturation moment was estimated by taking either the paramagnetic moment obtained from the Curie-Weiss law (with $T=5$ K, $C=1$, and θ estimated as above) or the ferromagnetic moment, approximated as $M_{sat}=1.6\ \mu_B-\frac{(1.6\ \mu_B)(100x)}{0.86}$, as was judged appropriate from our previous data on this system which showed that T_C extrapolates to zero at 86% Ca doping.[10] At each composition, λ was refined so that the high-temperature behavior of the simulated magnetization obeyed a Curie-Weiss law with $C=1$. While these calculations are not strictly derived from first principles results, the overall mean field magnetizations simulated in this manner closely resembled high-field bulk powder and single crystal magnetization data for a set of samples with widely varying saturation moments (1.6 to ~0 μ_B) and Curie-Weiss θ values (+150 to −100 K) in a system spanning a quantum phase transition.

III. RESULTS AND DISCUSSION

The low-temperature (5 K) Hall resistivity of the $Ca_xSr_{1-x}RuO_3$ system shows a stunning compositional dependence when the field dependence of the entire series is compared on a single plot (Fig. 1). A visual examination of the data shows two easily distinguishable regimes. At all compositions, there is a high-field regime where ρ_H varies linearly or nearly linearly in field. In ferromagnetic samples, there is a second regime where ρ_H is hysteretic and $\rho_{H\uparrow} \neq \rho_{H\downarrow}$ (the Hall resistivity measured with increasing and decreasing applied fields, respectively). It has been common practice in the literature to associate the jump in ρ_H in the hysteretic region with R_s and the slope of the H-linear regime with R_o, though these assumptions break down for systems such as $SrRuO_3$, where M_{sat} is not achieved at the maximal applied fields of the measurement (or even at fields of 40 T for most $Ca_xSr_{1-x}RuO_3$ compositions[14]). It can be seen that the slope of the H-linear region shows significant composition dependence. This slope is negative for <47% Ca, positive for samples with 47%–87% Ca, and again negative for

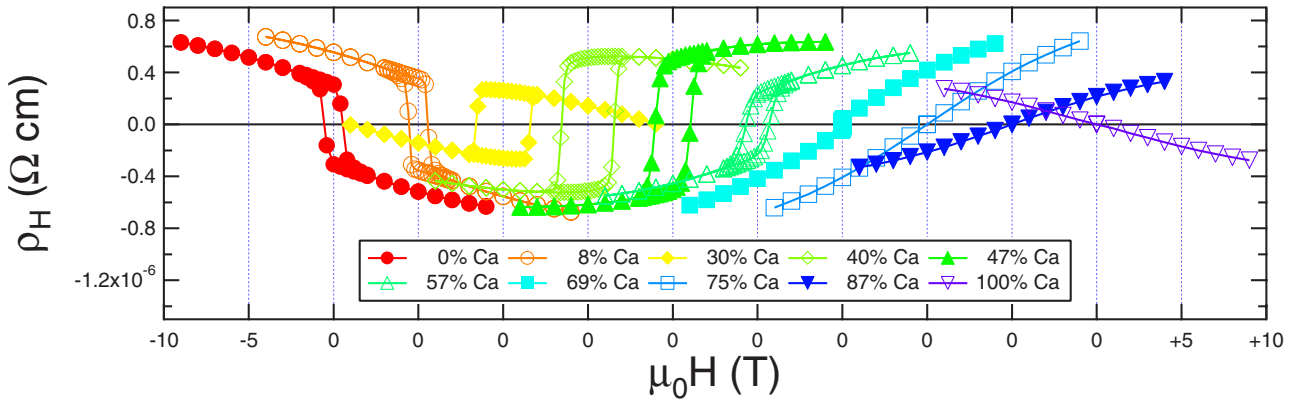

FIG. 1. (Color online) Compositional variation of the field-dependent Hall resistivity measured at 5 K for the $Ca_xSr_{1-x}RuO_3$ series. The origin of each sample is horizontally offset by 5 T from the previous composition for clarity. Dashed vertical lines indicate 5 T intervals.

the 100% Ca sample. In a simplistic interpretation, this would imply a change in carrier charge (electrons↔holes) as the boundaries between these three regions are crossed, an interpretation which does not apply here since the sample magnetizations are not saturated.

The behavior of the hysteretic region also has a strong compositional dependence. The width of the hysteresis in ρ_H is simply that of the hysteresis in M for these samples. As seen in Fig. 2(a), the relatively small coercive field of pure $SrRuO_3$ (H_c=4 kOe) increases with doping to a maximum of about 16 kOe for samples with 30%–40% Ca, before again decreasing as the absolute magnitude of the moment on the Ru atoms goes to zero. In samples with ⩽20% Ca, there is a large drop in ρ_H accompanying the field-induced magnetization reversal (corresponding to a negative R_s), while more Ca-rich samples show the opposite effect (positive R_s). The sign of R_s at H=0 can be unambiguously assigned since R_oB=0, leaving $\rho_H = 4\pi M R_s$ in the absence of an applied field. The value of this "spontaneous" R_s is plotted as a function of composition in Fig. 2(b), definitely proving that at 5 K there is a crossover from negative values of R_s to positive values of R_s near 21% Ca.

The composition variation of the temperature-dependent Hall resistivity (at $\mu_0 H$=9 T) has a very systematic variation when the samples are grouped according to their ground state magnetism (Fig. 3). When ρ_H for the most ferromagnetic $Ca_xSr_{1-x}RuO_3$ samples ($x \leqslant 60\%$) are plotted together in Fig. 3(a), similar behaviors are observed. At elevated tempera-

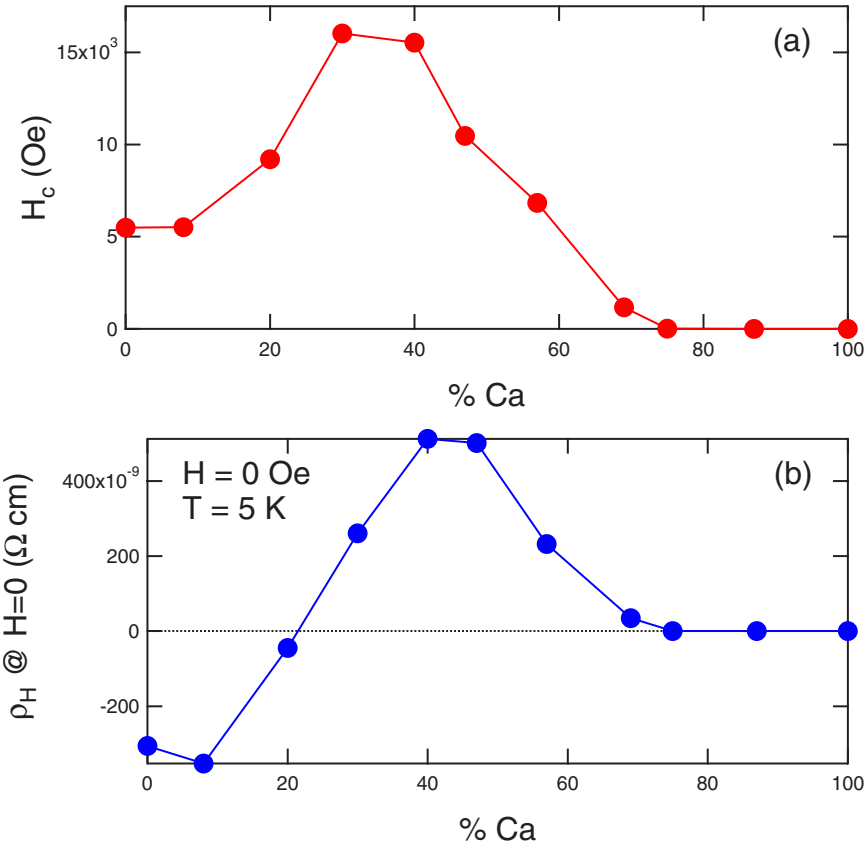

FIG. 2. (Color online) (a) Coercive field (H_c) obtained from measurements of ρ_H during field sweeps. (b) Spontaneous values of ρ_H measured at H=0 after first saturating the sample magnetization using a 90 kOe field.

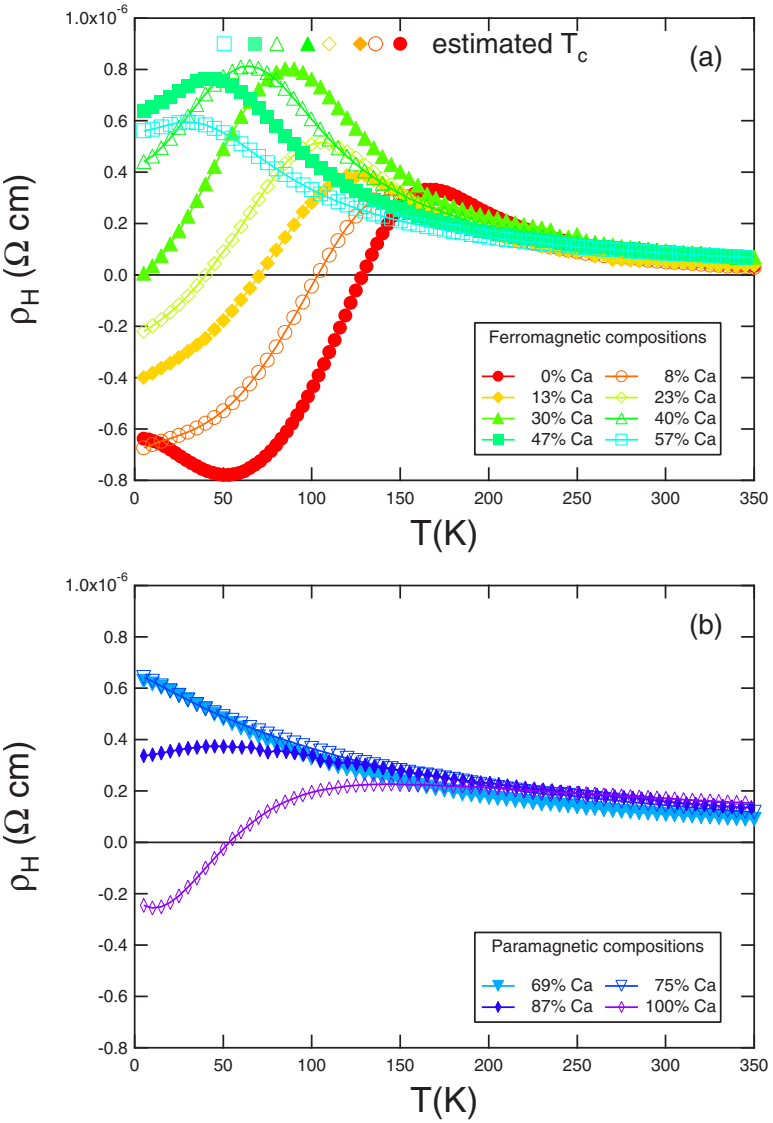

FIG. 3. (Color online) (a) Temperature dependence of ρ_H at $H=9$ T for ferromagnetic samples. Isolated symbols at top of the plot indicate the estimated T_C for each composition based on the linear relation previously observed in Ref. 11. (b) Temperature dependence of ρ_H at $H=9$ T for barely ferromagnetic or paramagnetic samples. Both plots are on the same scale.

tures, ρ_H increases on cooling until about T_C, at which point the slope of ρ_H vs T changes from negative to positive. This clearly indicates that the crossover in the behavior of ρ_H is associated with the ferromagnetic transition. This change is quite striking as the anomalous Hall response decreases despite M increasing on cooling. The highest values of ρ_H are found in the samples with 30% and 40% Ca. These maximal values are right around the crossover from the paramagnetic to the ferromagnetic regime, showing again that ferromagnetism serves to depress ρ_H in these samples. Between 20% and 30% Ca, the 5 K and 9 T value of ρ_H is negative despite the positive value of R_s. For these compositions, R_o must be negative (and larger in magnitude than R_s) and the carriers must be electrons. We can estimate the value of R_oB for the 30% Ca samples as at least -2.6×10^{-7} Ω cm by looking at the magnitude of R_s at $\mu_0H=0$ T, since $R_s4\pi M$ must be greater in magnitude at 9 T than at 0 T.

As we move toward the quantum phase transition (QPT) at 70%–75% Ca, the downturn in ρ_H is increasingly suppressed, and the two samples nearest the QPT no longer exhibit a downturn. The behavior of ρ_H for the paramagnetic samples (75%–100% Ca) is shown in Fig. 3(b). Curiously, as the system is tuned to the paramagnetic side of the QPT, ρ_H again begins to drop at low temperatures and even changes sign for the 100% Ca sample, exhibiting symmetric behavior around the QPT. Although the $CaRuO_3$ sign change has been commented on previously, its origin has still not been resolved. While the sign of R_s could unambiguously be determined for the ferromagnetic samples, there is no absolute method of deconvoluting the contributions of R_s and R_o in samples without magnetic ordering due to the lack of hysteresis. Frequency-dependent infrared Hall measurements are being pursued as an alternative method for answering this questions.[15,16]

We have additionally followed the detailed field (H) dependence of ρ_H for a selection of the $Ca_xSr_{1-x}RuO_3$ samples at a variety of temperatures (Figs. 4 and 5). The high-field slope of ρ_H vs H curves is often used to estimate R_o from Hall data, while the y intercept of the fitted lines is used to find the anomalous portion, $R_s4\pi M$, sometimes written as ρ'_{yx}. In such an analysis, R_s is a derived quantity which is highly dependent on the accuracy and validity of the fitting procedure. An examination of the data for the $Ca_xSr_{1-x}RuO_3$ system shows that for all of the compositions examined in

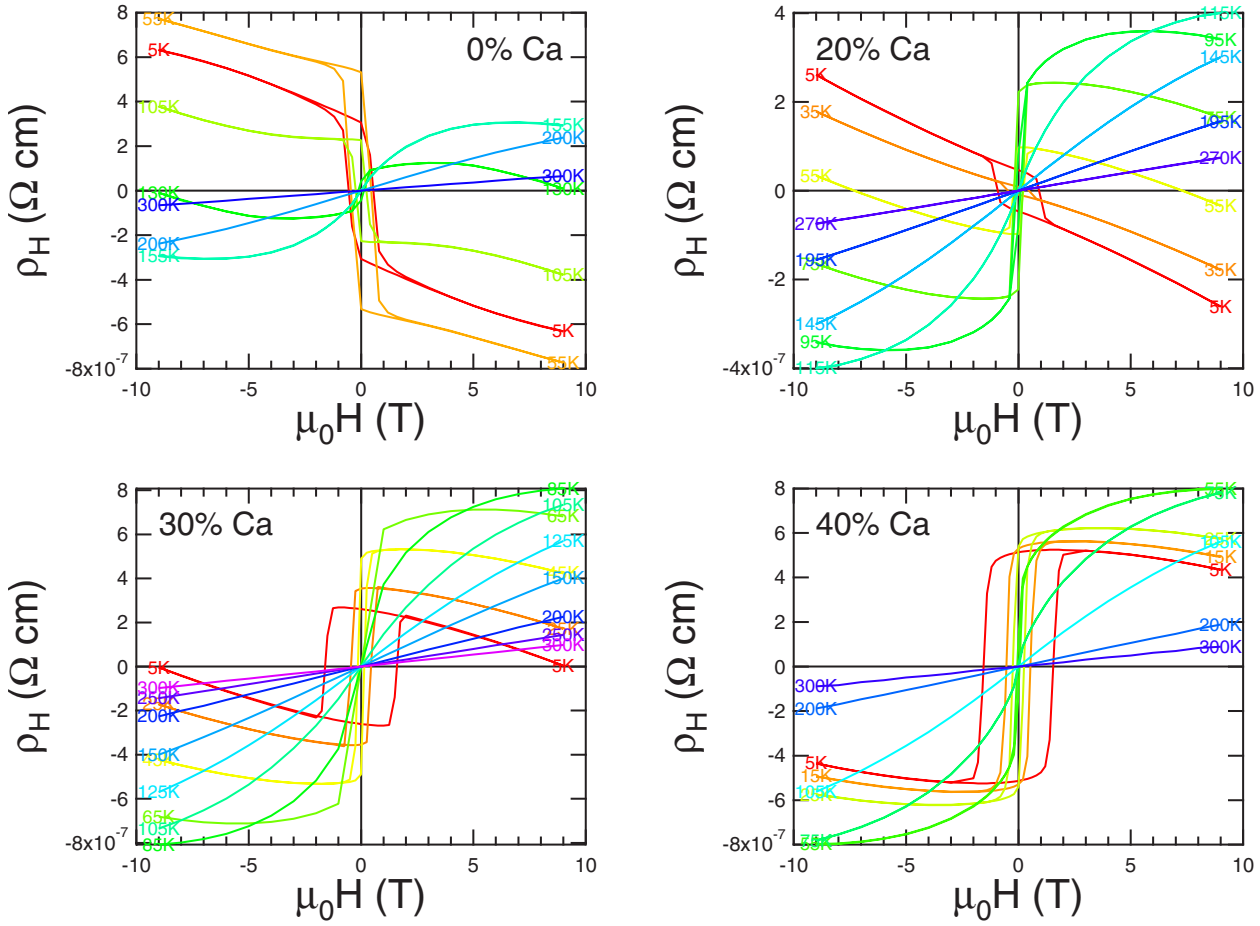

FIG. 4. (Color online) Field- and temperature-dependent Hall resistivities for samples with 0%, 20%, 30%, and 40% Ca. Temperatures are marked on scans, with colors varying from red (coldest, 5 K) to blue/violet (hottest, 250–300 K). Note the relatively small hysteretic steps at 5 K in the 20% sample, where R_s is near zero due to its proximity to a sign change. Significant variations in slope are observed even below T_C due to the inability of laboratory fields (9 T) to saturate the magnetism of these compounds.

detail, this high-field slope varies considerably with temperature, behavior that is not attributable to R_o (which should just scale with the carrier concentration). Furthermore, there is appreciable curvature in the ρ_H vs H plots even at high fields (9 T). These observations indicate a fundamental problem with applying this simple type of analysis to the $Ca_xSr_{1-x}RuO_3$ system of itinerant ferromagnets and make it difficult to readily obtain values of R_o. We have therefore chosen to display the unprocessed ρ_H rather than just the AHE portion (typically denoted as ρ_H^{AHE} or ρ_H') to eliminate model bias in the graphed data.

The difficulties in separating R_o and R_s are mainly due to the difficulty of fully saturating the magnetization within this $Ca_xSr_{1-x}RuO_3$ system, but they are also exacerbated by the similar magnitudes of the ordinary and anomalous Hall effect. This can be clearly seen in bulk susceptibility measurements of a 60% Ca sample (Fig. 6), where the sample magnetization increases by almost a factor of 2 between the closure of the hysteresis loop (at 1.5 T) and the extrapolated moment for a 9 T applied magnetic field. Furthermore, the unsaturated M increases nearly linearly with applied field even at 5 K in the high-field ferromagnetic regime. This means that both components of $\rho_H(=R_oB+R_s4\pi M)$ change linearly with applied field, making it impossible to separate the ordinary and anomalous portions of the Hall effect by using the common method of fitting the high-field portion of the ρ_H vs H data to a straight line.[17] This is a consequence of the either the itinerant nature of the magnetism or the strong magnetocrystalline anisotropy of the compounds in the $Ca_xSr_{1-x}RuO_3$ system. The only conditions where we can reasonably accurately estimate R_o from field sweeps are for the most magnetic samples at the highest fields. The slope of $SrRuO_3$ fit between 7 and 9 T gives a value of R_o of -2.53×10^{-12} Ω cm/G, or equivalently, -2.53×10^{-4} cm^3/C. From this number, we estimate a carrier concentration of 2.47×10^{22} electrons/cm^3. This is equivalent to 1.5 electrons per Ru site, based on the site density (1.69×10^{23} Ru/cm^3) estimated from the stoichiometry and reported lattice parameters. This carrier concentration is reasonably close to the values obtained in other studies[4,18] but is still somewhat surprising since an octahedral d^4 Ru ion might be expected to have holes as the dominant carriers because the t_{2g} band is more than half full. Under the 9 T fields used to measure ρ_H, R_oB is -2.27×10^{-7} Ω cm, only about a quarter of the largest magnitude of ρ_H found in our measurements in the $Ca_xSr_{1-x}RuO_3$ series.

Though it might seem that there is a special physical meaning for the compositions where the high-field slope of

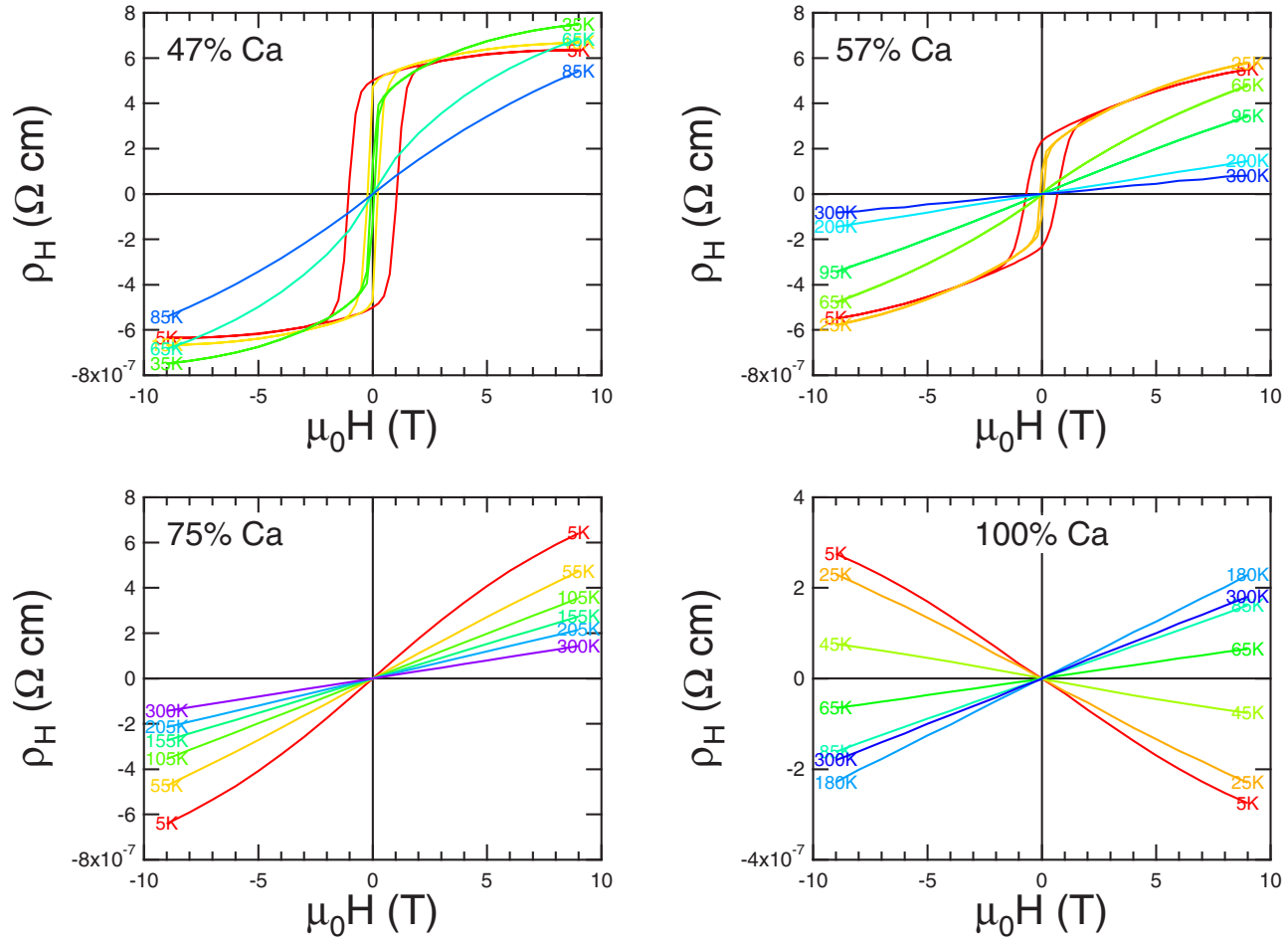

FIG. 5. (Color online) Field- and temperature-dependent Hall resistivities for samples with 47%, 57%, 75%, and 100% Ca. Temperatures are marked on scans, with colors varying from red (coldest, 5 K) to blue/violet (hottest, 85 K for 47% Ca, 300 K for all others). Nonlinear behavior and sign changes are observed even in the paramagnetic regime (75% and 100% samples).

the 5 K ρ_H hysteresis loops changes from negative to positive (around 47% Ca), this change is not due to a sign change in R_o. Instead, it reflects the point where R_o and $R_s\frac{dM}{dH}$ are equal in magnitude but opposite in sign. Since it is virtually impossible to accurately extract $\frac{dM}{dH}$ from magnetization measurements on thin films, the only statement that can be made with confidence is that the low-T values of R_o and R_s have different signs in the 47% Ca sample.

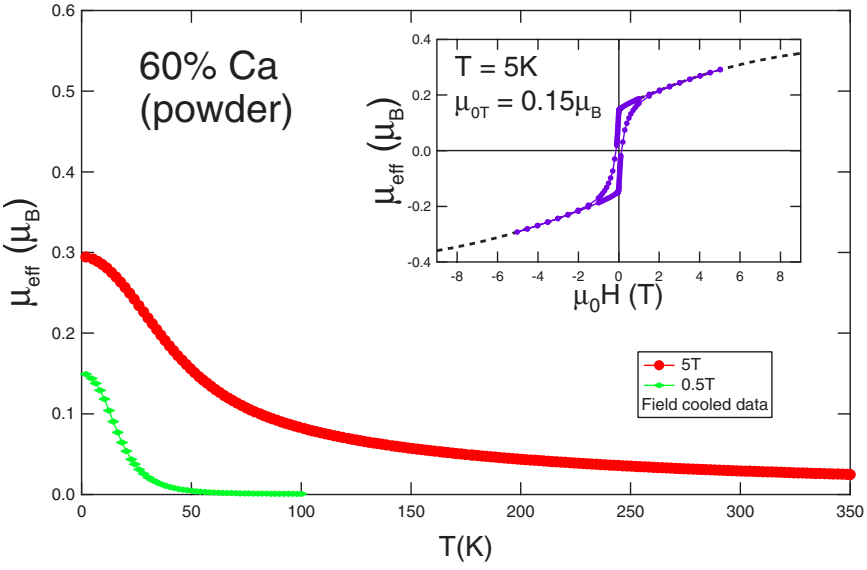

FIG. 6. (Color online) Temperature-dependent magnetization of a bulk preparation of a 60% Ca sample. Inset shows the field-dependent magnetization at fields up to 5 T. A parabolic fit (dashed line) was used to extrapolate the data to the Hall measurement field of 9 T.

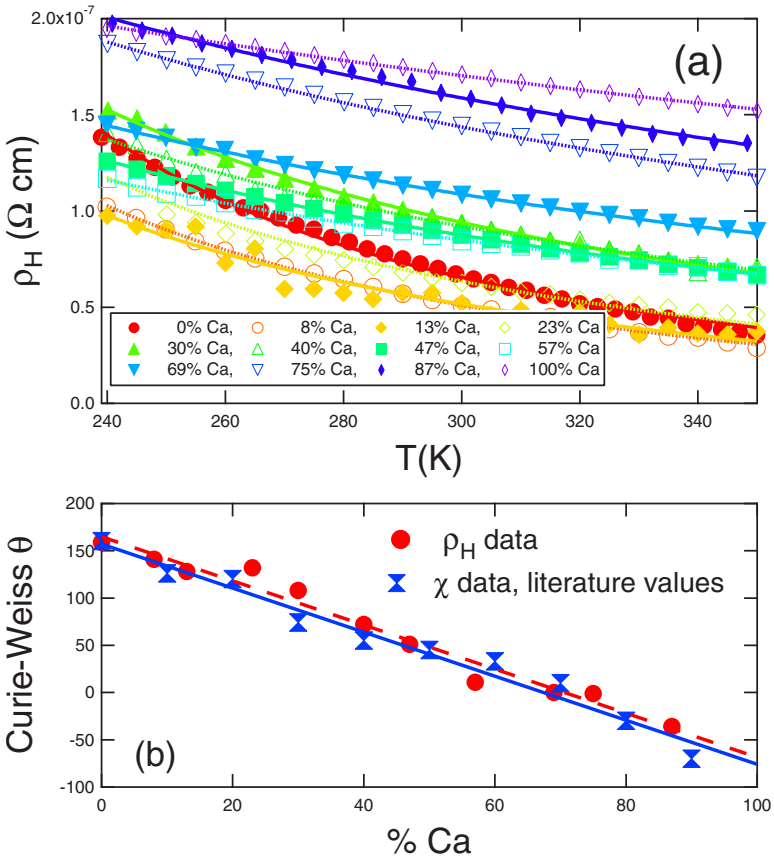

FIG. 7. (Color online) (a) Global fits of $\rho_H = \rho_0 + C_H/(T-\theta)$, with ρ_0 constrained to be the same for all compositions. Data were collected at an applied field of 9 T. Symbols and colors are the same as in the previous plots, with markers indicating measured data and lines representing fits from the refined parameters. The refined global fit value of ρ_0 is -3.77×10^{-13} Ω cm/G. (b) Comparison of the values of θ obtained from ρ_H fits (circles) to those obtained from the magnetic susceptibility measurements (double triangles) of Kanbayashi (Ref. 13) on bulk samples. Best fitted lines (dashed for ρ_H, solid for χ) have been drawn through these points. Data for 100% Ca have been omitted from the lower panel due to the anomalously low value of θ (−234 K) obtained from ρ_H fits.

While the individual analyses of $Ca_xSr_{1-x}RuO_3$ samples are complicated by their nearly linear response of M to H under a wide range of conditions, stronger insights can be obtained when the series as a whole is examined. Across the entire range of $Ca_xSr_{1-x}RuO_3$ samples, the high-temperature behavior of ρ_H looks quite similar to the Curie-Weiss behavior of the magnetic susceptibility (χ) measured on bulk preparations in this system.[13] This is not surprising, as in the temperature regime in which the Curie-Weiss law is obeyed, $4\pi M = \chi H$, allowing us to rewrite our original expression for the Hall resistivity, $\rho_H = (R_o + R_s\chi)H$. In this regime, both the ordinary and anomalous contributions to ρ_H have an identical field dependence, and we cannot use field sweeps to separate the two components. If both R_o and R_s do not have a significant temperature dependence,[19] the T dependence of ρ_H will be the same as the T dependence of χ, which is well modeled by $\chi = C_{cw}/(T-\theta)$.[20] We can therefore fit the Hall resistivity data to a similar formulation, $\rho_H = R_oH + C_H/(T-\theta)$, and use temperature to separate the ordinary (first term) and anomalous (second term) contributions to ρ_H. Note that θ still corresponds to the Weiss coefficient describing the nature and strength of magnetic interactions, and $C_H = C_{cw}HR_s$. The Curie constant C_{cw} and applied field H are known to be T independent, while R_s is assumed to be independent or nearly independent of T in the high-temperature regime ($T > T_C$).

The validity of assuming a constant R_s can be tested by constraining R_o to be constant across all compositions in the $Ca_xSr_{1-x}RuO_3$ series while allowing C_H and θ to freely vary for each composition. Excellent fits are obtained when a global fit is performed on the data in the 240–350 K range [Fig. 7(a)], suggesting that R_s is essentially constant in the high-temperature regime. There is superb agreement between values of θ obtained from these fits and those reported previously[13] for bulk measurements on powder preparations of $Ca_xSr_{1-x}RuO_3$ samples [Fig. 7(b)]. The global fits give a value of R_o of 3.77×10^{-13} Ω cm/G, a value significantly lower than that obtained from other methods. This deviation may just be a mathematical mechanism for the global fit to compensate for the changes of R_s resulting from small variations (~20%) of ρ_{xx} in the fitting regime and seems to only approximate the true value of R_oB in this system. An alternative possibility is that R_o is not constant across the series and that the global R_o value represents an average across all compositions.

The single composition which is not well described by this Curie-Weiss-type fits is pure $CaRuO_3$, which in many ways shows the most unusual behavior of any compound in this series. Although the data are well fitted by the common carrier concentration, the fit θ_{CW} of −234 K falls far afield of the extrapolated value of −68 K from the line drawn through the data for other compositions. Even when not constrained to share the same R_o as the other compositions, an unreasonable value of θ (−350 K) is obtained. The inability of local and global fits to give a reasonable value for θ_{CW} in $CaRuO_3$ raises the possibility that the high-temperature carriers in this material are holes and not electrons. In their theoretical calculations, Mazin and Singh[21] found that exactly at the Fermi energy E_F, the carriers are electrons in $SrRuO_3$ and holes in $CaRuO_3$, though the influence of neighboring states might not make those findings representative of the material as a whole. Recent work[22] exploiting the anisotropic susceptibil-

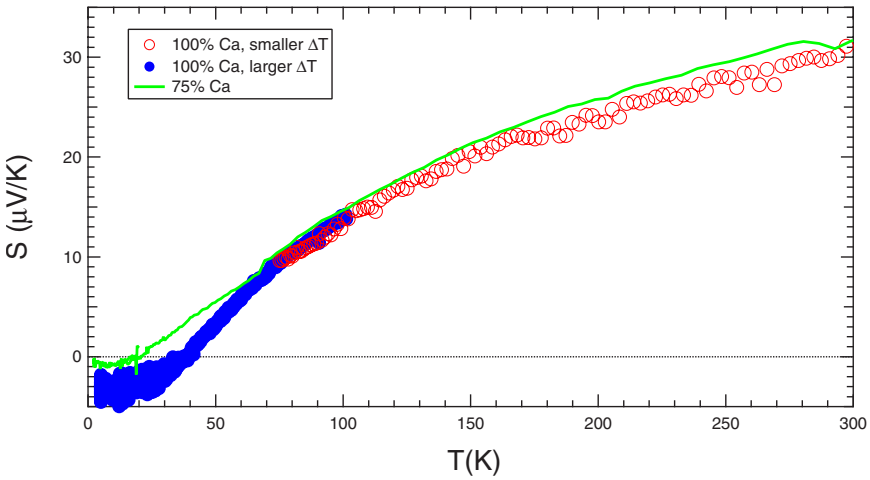

FIG. 8. (Color online) Seebeck coefficient for thin films with a composition of 75% Ca (solid line) and 100% Ca (circles) obtained from thin film measurements.

ity of thin film $CaRuO_3$ has extracted a hole carrier concentration which corresponds to $R_o = +2.6 \times 10^{-12}$ Ω cm/G, though the validity of this novel method has yet to be externally confirmed. It appears that either R_o or R_s has a very significant temperature dependence for this one composition, though it is impossible to tell which one at this time. As seen in Fig. 8, the Seebeck coefficient (S) of $CaRuO_3$ has a sign change at 40 K, not far from the sign change at 50 K for ρ_H, suggesting that the origin may be in R_o. This proof is far from conclusive for two reasons. The 75% Ca sample also exhibits a sign change in S, yet does not have a sign change in ρ_H. In addition, the positive sign of S obtained for $SrRuO_3$ in Seebeck measurements[23,24] implies the signs of the dominant carriers are holes, opposite of what was obtained from the Hall resistivity data.

Despite the fact that all $Ca_xSr_{1-x}RuO_3$ compositions exhibit a positive value of ρ_H at high temperatures, the OHE response is generally negative. Even the relatively small Curie-Weiss magnetization of these samples ($<0.1\ \mu_B$ at high T) is sufficient to generate an anomalous Hall effect of opposite sign and greater magnitude than the ordinary Hall effect, making fits of this type crucial to correctly understand the charge carriers in this system. We can get secondary proof that the dominant carriers are electrons by looking at ferromagnetic samples where R_s goes to zero as it changes sign. We can obtain the Hall coefficient R_H by dividing the Hall resistivity (ρ_H) through by field (H). This leads to the general expression $R_H = R_o + R_s 4\pi M/H$. In the ferromagnetic regime, the magnetic susceptibility M/H is expected to be strongly field dependent. If we find a temperature in the ferromagnetic regime at which R_H is independent of field, the value of R_s must be zero, and we will be trivially able to obtain the value for R_o. As seen in Fig. 9, this situation is realized for the 0% and 20% Ca samples at ~115 and ~30 K, respectively. By finding the value of R_H at the point where all of the R_H vs T curves cross, we roughly estimate that $R_o = -2.75 \times 10^{-12}$ Ω cm/G for the pure $SrRuO_3$ sample at 115 K and that $R_o = -2.25 \times 10^{-12}$ Ω cm/G for the 20% Ca sample at 30 K, numbers that are consistent with our original estimate of $R_o = -2.47 \times 10^{-12}$ Ω cm/G from field sweep data.

While we have been able to obtain a good estimate of R_o, we are most interested in learning about the temperature and field dependence of the anomalous portion, R_s. Rearranging our expression for the Hall resistivity, we find that $R_s = (\rho_H - R_o B)/4\pi M$. This can only be done if we get a good estimate of the sample magnetization under the conditions of the Hall measurements ($H = 9$ T). M from the thin films cannot be accurately measured since the contribution from the sample (~10^{-6} g) is not substantially larger than that of the diamagnetic substrate (~10^{-1} g), especially for Ca-rich samples which are not strong ferromagnets. Furthermore, the largest in-plane dimension of the thin film samples (~1 cm) precluded magnetic measurements in the same orientation as the Hall measurements. In order to consistently describe the susceptibility of the entire $Ca_xSr_{1-x}RuO_3$ thin film samples, we simulated the sample magnetizations using a semiempirical mean field (MF) model incorporating parameters obtained from bulk sample measurements. The simulated magnetizations are shown in Fig. 10 in units of emu/mol. The maximum magnetization ($SrRuO_3$ at low T) was 0.0992 emu/mol at 9 T, or equivalently, 3125 G.

Although MF theory, in general, suffers from the limitation that the Curie-Weiss θ and the magnetic ordering temperature T_C are constrained to be equal and is known to imperfectly model sample magnetization at low applied fields, the adaptability of the MF model makes it appropriate for this system. The lack of a sharp ordering feature in the 9 T susceptibility data and the similar magnitudes of the paramagnetic and ferromagnetic portions of the magnetic susceptibility at high fields allow both the low-temperature and high-temperature data to be reasonably modeled using a mean field theory using a single parameter (λ) for the strength of the internal magnetic interactions, where $H_{eff} = H + \lambda M$. The validity of this simulation for M is perhaps best assessed by examining the extracted values of R_s that it produces through the derived equation $R_s = (\rho_H - R_o B)/4\pi M$. In Fig. 11, we have drawn plots of R_s calculated using the low-temperature ferromagnetic estimate of $R_o B$ (-2.5×10^{-7} Ω cm).[25] The simulated mean field magnetizations lead to values of R_s which vary smoothly and simply with temperature, in sharp contrast to the complex temperature dependence of the measured ρ_H. This highlights the importance of using R_s rather than ρ_H to examine the anomalous Hall effect in magnetic materials.

The variation of the AHE with composition is also remarkably smooth. Despite the suppression of ferromagnetic

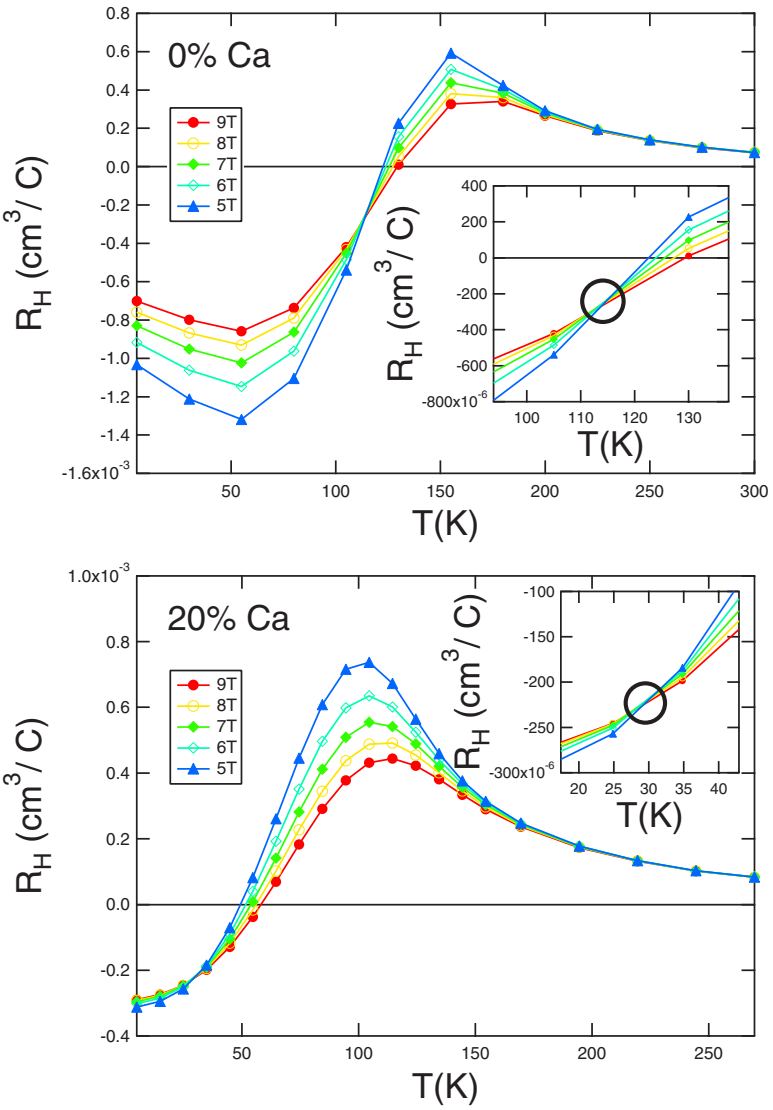

FIG. 9. (Color online) R_H data showing location of the sign change in R_s for samples with 0% Ca (~115 K, top) and 20% Ca (~30 K, bottom). Values of R_o found at these special points are in general agreement with the value refined from the Curie-Weiss fits despite the relatively large temperature step sizes. Measuring fields ranged from 5–9 T in 1 T steps.

interactions with increasing Ca doping, the high-temperature component of the anomalous Hall coefficient R_s is found to increase about fourfold on going from ferromagnetic $SrRuO_3$ to paramagnetic $CaRuO_3$. This underscores the fact that R_s describes a magnetotransport coupling constant which does not simply depend on the degree of magnetization or the strength of spin-spin coupling. The increase in R_s with Ca doping is essentially monotonic and shows mild and regular variation with concentration. This is in apparent contradiction to theoretical work which predicts that the AHE has a "sharp and spiky" variation with Fermi energy,[8] though the doping across the $Ca_xSr_{1-x}RuO_3$ series, of course, probes changes in sample electronic structure rather than changes in carrier concentration (since the Ca/Sr substitution is isoelectronic). We would welcome detailed calculations of the band structure of the full range of $Ca_xSr_{1-x}RuO_3$ samples and of their anomalous Hall response (in the form of σ_{xy}^{AHE}) to allow this assertion to be fully tested.

When examined in the context of the entire series, samples near the quantum phase transition (at 70%–75% Ca) have the smallest drops in R_s among the entire series. Samples further in composition from the quantum phase transition in either direction (toward ferromagnetism or toward paramagnetism) have larger drops in R_s. While the abrupt drops and sign changes in R_s for ferromagnetic samples appear to be related to changes which occur during ferromagnetic ordering, the origin of the large drop in R_s for $CaRuO_3$ is less clear. One intriguing possibility is that a hidden magnetic order develops on the paramagnetic side of the quantum phase transition in this system, resulting in behavior of the type observed in the closely related MnSi system.[26] The anomalously large magnetoresistance of $CaRuO_3$ at low temperatures[10] also supports this possibility. While not detectable in bulk susceptibility measurements, such hidden order may still affect R_s and would be consistent with the observation of symmetrical behavior in R_s on opposite sides of the QPT. Another possibility is that the nature of the carriers has a strong temperature dependence in $CaRuO_3$, though this is not consistent with the positive Hall coefficient reported for $CaRuO_3$.[22]

In conclusion, the compositional dependence of the sign changes in ρ_H at both ends of the $Ca_xSr_{1-x}RuO_3$ has been investigated and found to be only a feature of the end members, with an unexpected symmetry about the quantum phase

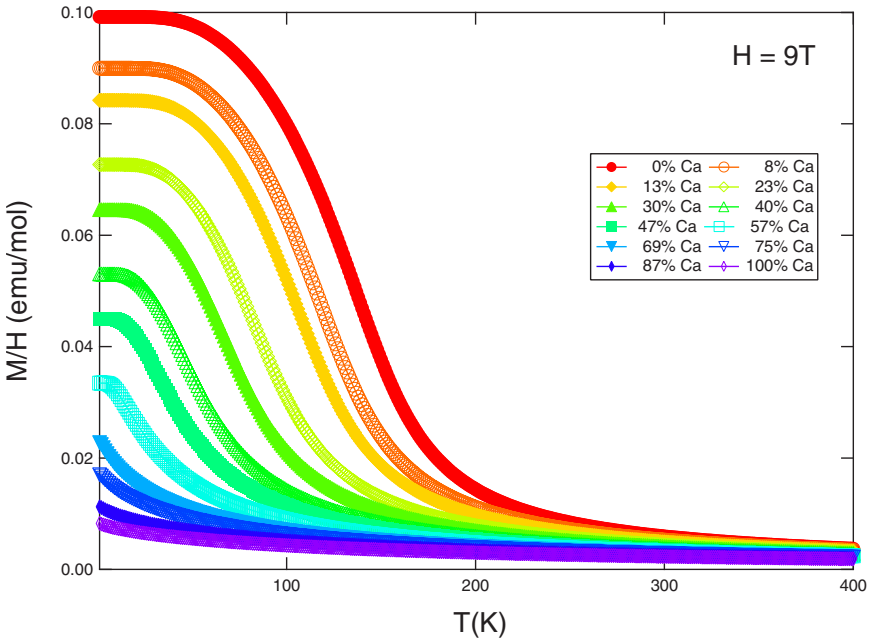

FIG. 10. (Color online) Simulated magnetic susceptibilities (at $H=9$ T) of samples in the $Ca_xSr_{1-x}RuO_3$ series.

transition in this series. The peaks in the temperature-dependent plots of Hall resistivities (ρ_H) seen for many members of the $Ca_xSr_{1-x}RuO_3$ series disappear when the data are normalized for sample magnetization and plotted in terms of R_s, indicating that the anomalous Hall response for these materials is a smoothly varying function of temperature. Even after this normalization, R_s still shows a pronounced transition at the ferromagnetic T_C (and a sign change below T_C for samples with $\leqslant$20% Ca). This indicates that there are fundamental differences between the values of R_s observed for ferromagnetic samples in the low-T regime ($T<T_C$, where R_s can change sign) and in the high-T regime ($T>T_C$, where R_s is always positive and varies smoothly with composition). This difference is ascribed to changes in the Fermi surface of these itinerant ferromagnets as a result of magnetic ordering. From the high-T behavior of R_s, it is concluded that the strongest anomalous Hall response (for a given sample magnetization) actually occurs for the paramagnetic and not ferromagnetic compositions, underscoring the complex nature of the anomalous Hall effect.

ACKNOWLEDGMENTS

We would like to acknowledge insightful discussions on this work with A. Millis, Q. Niu, and D. Singh. This research is sponsored by the U.S. Department of Energy under Contract No. DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, and at Buffalo, by the Research Corporation and NSF-CAREER-DMR0449899.

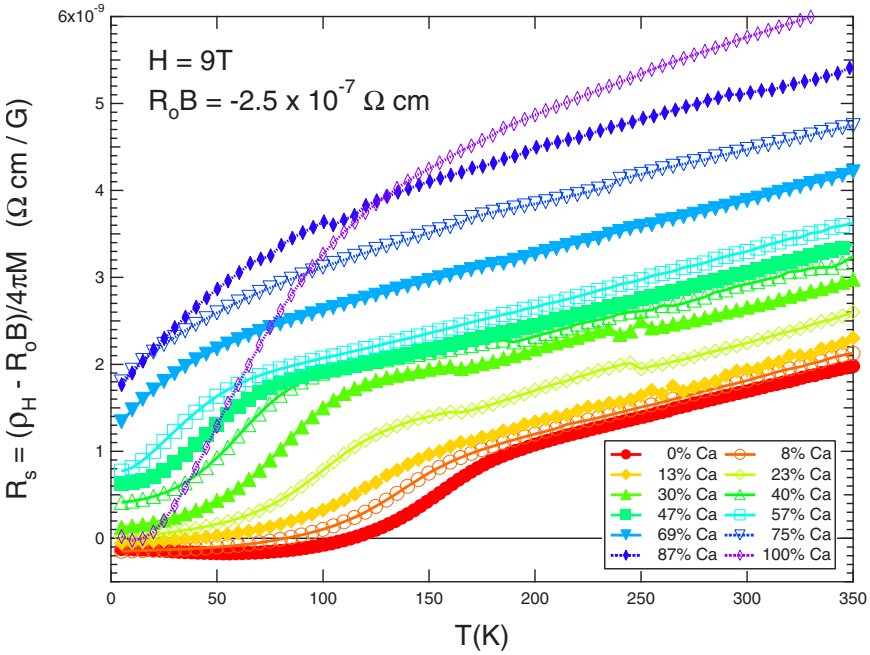

FIG. 11. (Color online) Variation of R_s as a function of composition and temperature in the $Ca_xSr_{1-x}RuO_3$ series, measured at $H=9$ T with R_oB set at the value obtained from ferromagnetic samples at low temperatures.

[1] *The Hall Effect and Its Applications*, edited by C. L. Chien and C. R. Westgate (Plenum, New York, 1980).

[2] The quantity σ_{xy}^{AHE} is still M dependent and is best compared to theory when M is saturated.

[3] B. C. Sales, R. Jin, D. Mandrus, and P. Khalifah, Phys. Rev. B **73**, 224435 (2006).

[4] M. Izumi, K. Nakazawa, Y. Bando, Y. Yoneda, and H. Terauchi, J. Phys. Soc. Jpn. **12**, 3893 (1997).

[5] H. C. Yang, S. H. Liu, L. M. Wang, and H. E. Horng, J. Appl. Phys. **85**, 5792 (2006).

[6] S. C. Gausepohl, M. Lee, R. A. Rao, and C. B. Eom, Phys. Rev. B **54**, 8996 (1996).

[7] G. Cao, S. McCall, M. Shepard, J. E. Crow, and R. P. Guertin, Phys. Rev. B **56**, 321 (1997).

[8] Z. Fang, N. Nagoasa, K. S. Takahashi, A. Asamitsu, R. Mathieu, T. Ogasawara, H. Yamada, M. Kawasaki, Y. Tokura, and K. Terakura, Science **302**, 92 (2003).

[9] Y. Yao, L. Kleinman, A. H. MacDonald, J. Sinova, T. Jungwirth, D. Wang, E. Wang, and Q. Niu, Phys. Rev. Lett. **92**, 037204 (2004).

[10] P. Khalifah, I. Ohkubo, H. M. Christen, and D. G. Mandrus, Phys. Rev. B **70**, 134426 (2004).

[11] I. Ohkubo, H. M. Christen, S. Sathyamurthy, H. Y. Zhai, C. M. Rouleau, D. G. Mandrus, and D. H. Lowndes, Appl. Surf. Sci. **223**, 35 (2004).

[12] For a system of noninteracting spins with angular momentum J, the net magnetization of the system can be obtained by considering the thermal (Boltzmann) excitations within the $2J+1$ equally spaced energy levels (Ref. 27) and the fractional magnetization is described by the Brillouin function $B_J(x) = \frac{2J+1}{2J} \coth \frac{2J+1}{2J}x - \frac{1}{2J} \coth \frac{1}{2J}x$. The fraction of spins aligned with an applied external field H is dependent on only the ratio H/k_BT, as given by the formula $\frac{M}{M_{sat}} = B_J\left(M_{sat}\frac{H}{k_BT}\right)$. For ferromagnets, there is both a real external field and a fictitious internal field (which accounts for the tendency of spins to coalign or antialign), and we assume that each spin experiences a total field of $H_{eff} = H + \lambda M$. For small values of B_J (applicable to the high-temperature regime of the $Ca_xSr_{1-x}RuO_3$ samples), this expression reduces to the well-known Curie-Weiss law. If we know the temperature (T) and the applied field (H), we can numerically solve for the magnetization using the relation $M/M_{sat} = B_J\left(\frac{g\mu_B J}{k_BT}H + \frac{\theta}{T}\frac{3J}{J+1}\frac{M}{M_{sat}}\right)$ obtained from the Curie-Weiss parametrization.

[13] A. Kanbayashi, J. Phys. Soc. Jpn. **44**, 108 (1978).

[14] T. Kiyama, K. Yoshimura, K. Kosuge, H. Mitamura, and T. Goto, J. Phys. Soc. Jpn. **68**, 3372 (1999).

[15] M.-H. Kim, G. Acbas, M.-H. Yang, I. Ohkubo, H. Christen, D. Mandrus, M. A. Scarpulla, O. D. Dubon, Z. Schlesinger, P. Khalifah, and J. Cerne, Phys. Rev. B **75**, 214416 (2007).

[16] J. Cerne, D. C. Schmadel, L. B. Rigal, and H. D. Drew, Rev. Sci. Instrum. **74**, 4755 (2003).

[17] One promising technique for separating the H-dependent and M-dependent portions of ρ_H has been reported by Kats *et al.* (Ref. 28). However, this technique requires samples with strong magnetocrystalline anisotropy and is therefore only applicable to a subset of magnetic systems.

[18] L. Klein, J. R. Reiner, T. H. Geballe, M. R. Beasley, and A. Kapitulnik, Phys. Rev. B **61**, R7842 (2000).

[19] The substitution of Ca for Sr is isoelectronic, and ρ_{xx} only varies by about 20% in the temperature range of the fits.

[20] While a modified Curie-Weiss law $[\chi = \chi_0 + C_{cw}/(T-\theta)]$ is often used to model magnetic susceptibility, we choose to omit the χ_0 term due to its generally small magnitude, and because it is not clear that temperature-independent Pauli paramagnetism will generate an anomalous Hall response in the Berry's phase model of the AHE.

[21] I. I. Mazin and D. J. Singh, Phys. Rev. B **56**, 2556 (1997).

[22] M. Schultz, L. Klein, J. W. Reiner, and M. R. Beasley, Physica B **378-380**, 490 (2006).

[23] T. Maekawa, K. Kurosaki, H. Muta, M. Uno, and S. Yamanaka, J. Alloys Compd. **387**, 56 (2005).

[24] Y. Klein, S. Hebert, A. Maignan, S. Kolesnik, T. Maxwell, and B. Dabrowski, Phys. Rev. B **73**, 052412 (2006).

[25] The value of R_oB (-2.5×10^{-7} Ω cm) obtained through a fit of ρ_H vs H is undoubtedly the most accurate estimate for the most ferromagnetic samples, since it is confirmed in the analysis of Fig. 9. However, it differs by almost an order of magnitude from the value of R_oB (-3.4×10^{-8} Ω cm) obtained from the global Curie-Weiss-type fits across the entire series. If R_s is instead calculated using the global fit value, the temperature dependence of R_s at high temperatures (>200 K) flattens out, but is otherwise qualitatively very similar.

[26] C. Pfleiderer, D. Reznik, L. Pintschovius, H. v. Lohneysen, M. Garst, and A. Rosch, Nature (London) **427**, 227 (2004).

[27] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders College Publishing, Fort Worth, 1976).

[28] Y. Kats, I. Genish, L. Klein, J. W. Reiner, and M. R. Beasley, Phys. Rev. B **70**, 180407(R) (2004).