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Thermally excited spin-disorder contribution to the resistivity of $LaCoO_3$

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We have investigated the effect of the thermally induced spin-state transition on the electronic conduction mechanism in the perovskite $LaCoO_3$. The magnetotransport properties of this material are greatly influenced by this well studied spin-state transition. In fact, the excitation to a finite Co ion spin results in a *thermal activation of spin disorder*. This spin disorder is induced by thermal population of the nonzero spin states of the Co ions in zero magnetic field. The disorder is suppressed by a magnetic field leading to significant negative magnetoresistance effects, which are in effect thermally excited. We suggest that this material is an ideal testing ground for colossal magnetoresistive phenomena in a system where the complicating effects of lattice and magnetic phase transitions are not present.

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$LaCoO_3$ is unique amongst the series $LaMO_3$ (where M is a transition metal) in that it undergoes spin-state transitions with increasing temperature, a property that has received considerable attention recently.[1] In essence this compound lies in very close proximity to the situation where the crystal-field energy and the Hund's rule exchange energy are identical. In fact, the crystal-field energy dominates over the Hund's energy so marginally that thermal energies of the order of a few meV can induce excitation across a ''spin gap.'' [1] Specifically, the ground state has Co^{3+} ions in the $3d^6$ configuration which form the $S=0, t_{2g}^6 e_g^0$ singlet state. Due to the fact that the crystal-field energy (E_{cf}) is only marginally larger than the Hund's exchange energy (H_{ex}), input of thermal energy ($\sim k_B T$) can lead to occupation of higher spin states. The Co ion transits to a finite spin state at around 90 K, resulting in a steep increase in the magnetic susceptibility[1–4] and the onset of paramagnetism.[5–8] The exact nature of the various Co ion states, and in fact the magnitude of the spin, is a matter of some controversy.[1–8] Early reports suggested that the system undergoes a transition from $S=0$ to $S=2$ (i.e., low spin to high spin) at 90 K (Ref. 5) while other authors suggested that two spin-state transitions take place from $S=0$ to $S=1$ (i.e., low spin to intermediate spin) at 90 K, followed by a further transition to the high spin state at 500 K (Ref. 3). An in-depth theoretical study[9] shed great light on the situation by showing that the intermediate spin-state model is favored ($S=1, t_{2g}^5 e_g^1$), while the magnetic anomaly at 500 K [and the coincident metal-insulator transition (MIT)] could be explained by the melting of an orbitally ordered state. This was followed by a further theoretical investigation[10] which also concluded that this compound is always in the $S=1$ intermediate spin state above 80 K. Theoretically the spin gap is thought to be of the order of 240 meV,[9] while experimental analysis of the temperature dependence of susceptibility suggests values in the range 25–35 meV.[2,4] The experimentally observed crossover from $S=0$ to $S=1$ occurs at approximately 80 K,[1–8] while theory predicts 150 K,[9] in reasonable agreement.

One of the most striking aspects of the behavior of this material is that the spin-state transition at ~80 K is thought to have no effect on the transport properties of the material.[1] This would appear unusual given that these perovskite materials exhibit a strong interplay between the conduction mechanism and the localized magnetic moments, and that the second apparent spin-state transition at 500 K is accompanied by a MIT.[1] In this work we show that the 80 K spin-state transition in fact has a large effect on the magnetotransport properties of $LaCoO_3$. The unusual spin-state transition leads to a situation where one can thermally excite spin disorder, which has a strong effect on the zero field resistivity. This thermally excited spin disorder contribution is suppressed by a strong magnetic field leading to considerable negative magnetoresistance (MR) of the order of 10%. This is in effect ''thermally excited'' colossal MR (CMR) type behavior, a phenomenon unique to this system. The impact of our work is that it unveils a material for CMR-type studies where the complicating effects of intertwined lattice and magnetic transitions (as is often the case in manganites[11,12]) are not present.

Polycrystals of $LaCoO_3$ were fabricated by the conventional solid-state reaction method. ''Four nines'' powders of La_2O_3 and Co_3O_4 (−80 mesh) were ground together and reacted at 1000 °C for one week. The progress of the reaction was continually monitored by removing a small amount of reaction product and performing x-ray diffraction (XRD). The product was then reground, pressed at room temperature under 50 kpsi into a disc, and then sintered at 1500 °C for 24 h. The final cooling step from 1500 °C to room temperature took place over 8 h. The material was characterized by XRD, iodometric titration, scanning electron microscopy, and electron microprobe analysis. The samples were found to be single-phase polycrystals with large grains of the order of 10 μm in size. Moreover, the compositional fluctuations were below the sensitivity limit of the electron microprobe analysis (6% in the La/Co ratio). Iodometric titration confirmed that the oxygen stoichiometry was extremely close to the nominal $LaCoO_3$ composition, being $LaCoO_{2.96\pm0.05}$.

Magnetometry measurements were performed from 5 K up to 300 K in magnetic fields up to 5 T in a commercial superconducting quantum interference device system and from 400 K up to 800 K in a vibrating sample magnetometer. The magnetotransport measurements were made from 50 to 700 K in magnetic fields up to 9 T using standard dc tech-

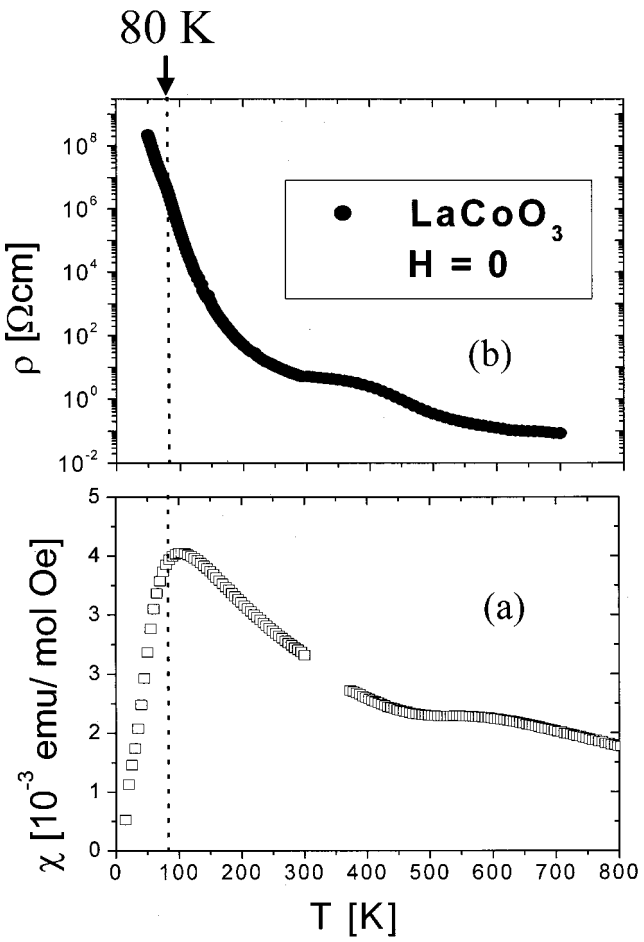

FIG. 1. Temperature dependence of (a) the magnetic susceptibility and (b) the electrical resistivity of $LaCoO_3$. The resistivity data were taken in zero magnetic field while the susceptibility data shown here were taken in 50 kOe. Note that the magnetization was linear in magnetic field in the whole temperature region studied. A small low-temperature "Curie tail" has been subtracted from the susceptibility data. The dotted line denotes the 80 K spin-state transition.

niques in a van der Pauw configuration. Below room temperature we used In metal as a contact material while above room temperature we used a high-temperature silver loaded epoxy. The contacts were Ohmic, and of negligible resistance in comparison to the sample, down to 50 K. (Care was taken to ensure that the effects of sample self-heating were negligible. This was done by measuring repeated $V-I$ curves at low T, measuring with various current levels and working only in the Ohmic regime. The dissipated power was well below safe levels for He^4 temperatures.) During magnetic field sweeps at temperatures of the order of 100 K the temperature stability was around 3 mK.

Figure 1 summarizes the temperature dependence of the susceptibility and resistivity in $LaCoO_3$. As observed previously, the susceptibility is very low at low temperatures and shows two clear anomalies with increasing temperature (80 K and 500 K).[1–8] The origin of these two anomalies was discussed above although it is clear from many previous works that the sharp increase in susceptibility at 80 K is the transition from $S=0$ to $S=1$.[1–8] The behavior of the resistivity, which is also consistent with previous work, shows semiconducting behavior as $T\rightarrow 0$ K, along with a broad decrease at ~500 K, coincident with the magnetic anomaly.[13] The overall semiconducting behavior is consistent with the prior classification of this material as a narrow band-gap semiconductor. The most interesting aspect of the data, which is only accessible in this work due to the extension of the measured temperature range below 100 K, is the small anomaly in the slope of the resistivity curve near 80 K. This is far more clearly observed in a $\ln(\rho)$ vs $1/T$ plot (Fig. 2) where it is revealed as a distinct change in transport properties at 80 K. This is rather close to the spin-state transition temperature and is in excellent agreement with the peak in the susceptibility in Fig. 1(a). Force fitting to simple activated behavior in the two regions gives $E_1=146$ meV at high temperatures and $E_0=38$ meV below 80 K. It is important to note that the limited temperature range (from 80 to 50 K) makes any attempt to determine the exact functional form of $\rho(T)$ ambiguous. Hence it does not seem possible to determine whether variable range hopping laws would better describe the low-temperature data.

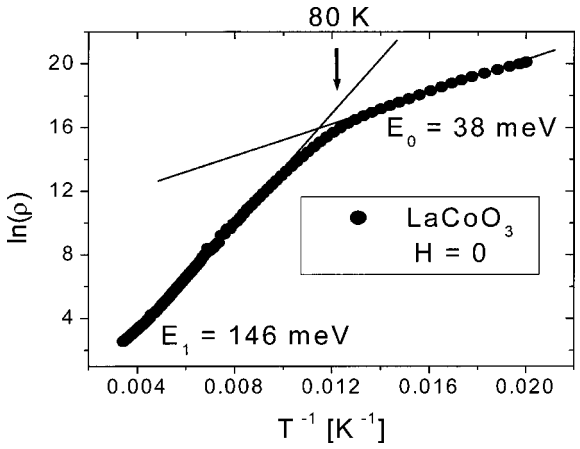

FIG. 2. Temperature dependence of the zero magnetic field resistivity plotted as $\ln(\rho)$ vs T^{-1}. The temperature range is from 300 K to 50 K. The resistivity became unmeasurably large below 50 K. The activation energies extracted from a "force fit" to $\rho=\rho_0\exp(E/k_BT)$, E_0 and E_1, are 38 meV and 146 meV, respectively.

The interplay between the conduction mechanism and the magnetic behavior is further elucidated by the behavior of the magnetoresistance as shown in Fig. 3. The 90 kOe MR [defined as $(\rho(H)-\rho(H=0))/\rho(H=0)$] starts from a positive value (~2.5%) at the lowest temperatures measured, crosses over to negative values with increasing temperature and reaches a peak (~8%) at 80 K. Note again that this is the same temperature as the peak in the magnetic susceptibility and the same temperature as the crossover in activation energies in zero magnetic field. Isothermal magnetic field sweeps are shown in Fig. 4 in the temperature region of interest around 80 K, along with a representative magnetization vs field curve at 100 K. Note that the negative MR effects do not saturate up to 90 kOe, consistent with the lack of saturation of the sample magnetization in this temperature range. In fact, the magnetometry data show no sign of satu-

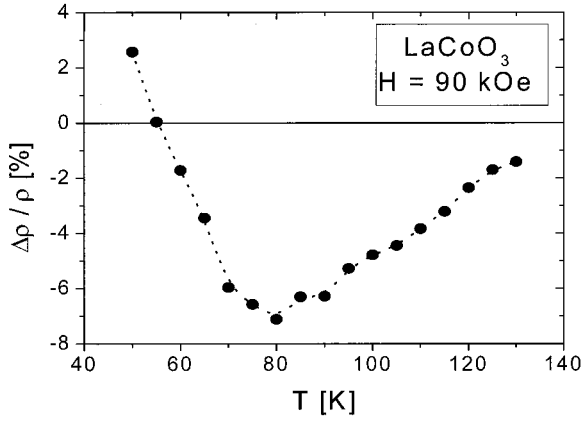

FIG. 3. Temperature dependence of the 90 kOe magnetoresistance. These data were obtained from two temperature sweeps—one in 90 kOe and one in zero field.

ration, and simple paramagnetism in the whole temperature range below 300 K.[14]

The low-temperature ($T \sim 50$ K) positive MR effects and the higher-temperature (>80 K) negative MR effects are further contrasted by their angular magnetic field dependencies. The negative MR effects are isotropic with respect to the angle between the current and the applied magnetic field, while the low-temperature positive MR is very sensitive to whether the magnetic field is applied in the sample plane (and therefore parallel to the magnetic field direction) or perpendicular to the plane. This is illustrated in Fig. 5, which shows $\ln[\rho/\rho(H=0)]$ vs H^2 in these two geometries. The MR is found to obey an $\exp(H^2)$ dependence (as expected for phonon assisted nearest neighbor, or variable range, hopping)[15] with the magnetic field perpendicular to the current, but disappears when the current is applied parallel to the magnetic field vector, a clear signature of an orbital MR effect. This behavior is well known as an ''acid test'' for hopping conduction as the conventional nonmagnetic wave function shrinkage leads to a positive MR when the field is perpendicular to the sample plane but has no effect on the conduction when the field is applied in plane. This is due to

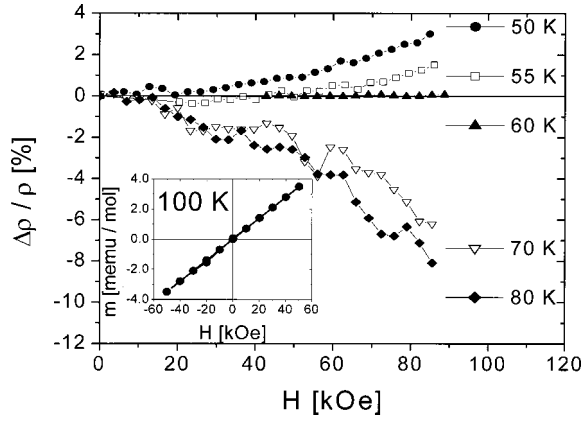

FIG. 4. Isothermal magnetoresistance vs magnetic field curves from 50 K to 80 K. The inset shows the field dependence of the magnetization at 100 K up to 50 kOe.

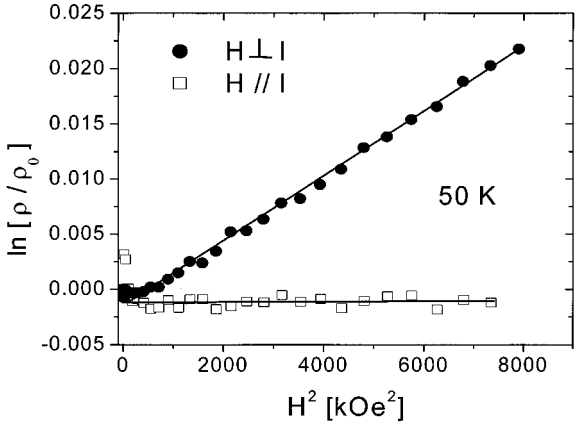

FIG. 5. Orientation dependence of the 50 K positive magnetoresistance effect. The two data sets shown are for the field perpendicular to the current direction and for the field parallel to the current direction. The current is in the sample plane. Note that the data are plotted as $\ln[\rho/\rho(H=0)]$ vs H^2 to allow a comparison to the theory for magnetoresistance in the hopping regime.

the fact that diamagnetic wave function shrinkage, which reduces the overlap between neighboring sites and increases the resistivity, has no effect when the direction in which the overlap is reduced is perpendicular to the measuring current. It is therefore clear that, although our $\rho(T)$ data are insufficient to discern between various forms of hopping conduction, hopping is indeed the active conduction mechanism at low temperatures. Note that a crossover from a nearest neighbor hopping MR regime to spin dependent MR effects on *decreasing* temperature is to be expected and has been observed previously in diluted magnetic semiconductors,[16] but we have observed a crossover to spin dependent MR with *increasing* temperature.

In summary, we observe a distinct change in conduction mechanism at the spin-state transition temperature which is accompanied by the onset of a large negative MR effect. This negative MR effect is isotropic, in contrast to the small positive MR effects observed at low temperatures which were demonstrated to be of ''nonmagnetic'' origin. Moreover, these isotropic negative MR effects show no saturation up to 90 kOe, consistent with the lack of saturation of the magnetization, which is the expected behavior in a weakly interacting paramagnetic system at these temperatures. Our explanation for this set of phenomena is simple. We explicitly assume that the observation of a distinct change in conduction mechanism and a distinct change in MR behavior at a temperature very close to the spin-state transition temperature is not coincidental. In essence, we are observing a thermally excited spin disorder contribution to the resistivity of $LaCoO_3$. As the temperature is increased from $T=0$ K and approaches 80 K an increasing fraction of the Co ions are excited into the $S=1$ state which results in the steady increase of the susceptibility. In zero magnetic field these spins are randomly aligned and the system has zero magnetization. This situation results in a spin disorder contribution to the resistivity. However, when a magnetic field is applied the Co spins are aligned and the spin disorder contribution is suppressed, leading to a simple negative MR effect. Note that

this naturally explains the lack of saturation of the negative MR (the magnetization itself is not saturated) as well as the isotropic nature of the MR. In a simple metallic system one would describe this as field induced suppression of the spin disorder scattering but in a semiconducting system such as this it is clear that the conduction mechanism is not simply diffusive. In fact, we already know from the low-temperature orbital MR effect that a hopping conduction mechanism is active. Our simple scenario of a field induced suppression of spin disorder is still valid although in this case the magnetic field reduces the spin disorder part of the disorder potential and effectively increases the probability for a nearest neighbor hop. This is a similar concept to that used in the work on the classic $Gd_{3-x}v_xS_4$ (v=vacancy) magnetic semiconductor system (see Ref. 11, p. 184 for example). The most important aspect of our observed effect is the thermal excitation of the spin disorder; the qualitative model for explaining negative MR in terms of field suppression of the spin-disorder part of the random potential has been often used in the past.[11,17]

It is worth noting that the effects we observe are essentially thermally excited CMR type effects. In other words, we are provided with a perovskite system where the negative MR can be studied in a situation where complicated effects of coupled lattice, electronic and magnetic transitions are not present. This is often the case in the manganites, for example, where the CMR effects are observed in the vicinity of a magnetic phase transition, an MIT and, in some cases, a structural change.[11]

The final point to be addressed is the origin of the two activation energy values we observe. It is intriguing to note that the apparent low T activation energy is very close to the experimentally determined values of the spin gap ($\sim$30 meV) and it seems natural to claim that this conduction process is intimately related to the spin gap. Golovanov, Mihaly, and Moodenbaugh[18] suggested that the conduction at low temperature in this material is likely to involve activation across the spin gap followed by double exchange between the Co^{4+} and Co^{3+} ions. This would naturally explain the equivalence of the spin and charge gap energies at low temperatures and adds further weight to our argument that this material shows a strong interaction between the spin and charge degrees of freedom. Clearly the simple activated behavior at $T>80$ K, where the Co ions are primarily in the $S=1$ state, must be due to a different mechanism, the origin of which remains unclear. It is tempting to simply interpret this activation energy (150 meV) as activation across the band gap. Previous optical measurements have deduced that the band gap is in excess of 0.1 eV although it is difficult to determine directly due to the broad onset of conductivity with increasing frequency.[19,20] Theoretical estimates lie in the 2 eV range although the calculational method used (local-density approximation+U) is known to overestimate band gaps. It seems that ascribing the 150 meV activation energy to the band gap is not unfeasible although it could equally likely be due to activation from a dopant level residing within the intrinsic band gap, or hopping conduction. An accurate determination of the band gap in this system is urgently required. In any case the negative MR effect must stem from suppression of spin disorder by a magnetic field. To make more conclusive statements about the exact MR mechanism one would need to understand more fully the conduction process above 80 K.

In summary, we have observed a thermally excited spin disorder contribution to the resistivity of $LaCoO_3$. The thermal excitation of Co ions to the $S=1$ spin state leads to the creation of spin disorder in zero magnetic field which is suppressed by a large field, leading to negative magnetoresistance.

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