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Abstract. The temperature dependence of the static magnetic susceptibility χ_0 (5 to 700 K) and that of the electron paramagnetic resonance linewidth ΔH (300 to 700 K) measured at 9.25 GHz is reported for bulk polycrystalline samples of La$_{0.67}$Sr$_{0.33}$MnO$_3$ ($T_c = 375$ K) and La$_{0.62}$Bi$_{0.05}$Ca$_{0.33}$MnO$_3$ ($T_c = 238$ K) with negative giant magnetoresistance. For both systems, ΔH and the product $\Delta H \chi_0 T$ increase linearly with temperature above T_c. Following the analysis of Huber and Seehra for CrBr$_3$, it is argued that this linear temperature dependence of $\Delta H \chi_0 T$ is most probably due to contributions from spin–phonon interaction. This result supports the recent suggestions of the importance of lattice effects in the magnetism of these oxides.

1. Introduction

The magnetotransport properties of the manganate perovskites La$_{1-x}$M$_x$MnO$_3$ (M = Ca, Sr, Pb, ...), have received enormous attention in recent years primarily because of the observation of giant magnetoresistance (GMR) below the Curie temperature T_c where an applied magnetic field produces a giant change in the electrical resistance [1, 2]. The magnetic properties of these perovskites were first investigated over forty years ago; that investigation showed them to become ferromagnetic for $x \simeq 0.2$ to 0.5, this change being accompanied by a semiconductor–metal-like transition near T_c [3–5]. The double-exchange model of Zener [4] and de Gennes [5] involving exchange of two electrons in Mn^{3+}–O^{2-}–Mn^{4+} and Mn^{4+}–O^{2-}–Mn^{3+} configurations provided reasonable explanations for both the ferromagnetism and the associated electrical conductivity. Subsequently, Leung *et al* [6] and Searle and Wang [7] carried out magnetic and transport studies on a single crystal of La$_{0.56}$Pb$_{0.44}$MnO$_3$ ($T_c \simeq 350$ K) for temperatures up to 425 K.

Recently, a number of research groups [8–10] have presented arguments showing that the 'double-exchange' model alone is not sufficient to explain the GMR effect of the manganate perovskites and that a strong spin–phonon interaction arising from the Jahn–Teller splitting of the Mn d levels plays an important role. If this is true, then a strong temperature dependence of the electron-paramagnetic-resonance (EPR) linewidth should be observed for $T > T_c$. This theory, developed by Huber and Seehra [11] for the ferromagnet CrBr$_3$ ($T_c \simeq 32$ K) applies to a certain class of concentrated magnets with strong spin–phonon coupling, resulting in a linear (quadratic) increase in ΔH with temperature if a single-phonon (two-phonon) process is dominant.

For the doped perovskites, the only reported EPR measurements have been those by Searle and Wang [7] and the more recent studies of Lofland *et al* [12]. The measurements of Searle and Wang limited to 425 K showed a minimum in ΔH near T_c ($\simeq$350 K), so ΔH increased both above and below T_c. The data of Lofland *et al* [12] are primarily for below T_c where they demonstrate that an increase in ΔH below T_c in ferromagnets is not intrinsic but can occur due to inhomogeneity of the magnetization across the sample. Another source of spurious increase of ΔH, also proportional to the magnetization, can be the sample size effect or cavity overloading [13] which can easily occur in ferromagnetic materials with large magnetization. Above T_c, both of these effects should be less serious problems since magnetization decreases rapidly with T for $T > T_c$. The above summary shows that a careful check of any temperature dependence of ΔH in the manganates, over an extended temperature range above T_c, is not yet available to check the contribution from spin–phonon interaction. In this paper we report a careful study of the temperature dependence of ΔH in polycrystalline bulk samples of $La_{0.67}Sr_{0.33}MnO_3$ and $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ for temperatures up to 700 K. A linear temperature dependence of the EPR linewidth is observed above T_c, which is argued to be due to spin–phonon interaction in the manganates.
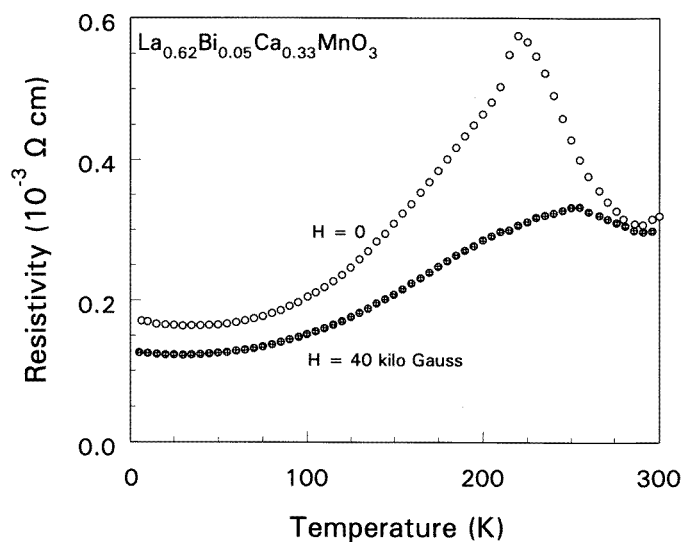

Figure 1. The temperature dependence of the measured electrical resistivity for $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ with the applied magnetic fields $H = 0$ and $H = 40$ kG. The applied field H is parallel to the electrical current.

2. Experimental details

The EPR measurements were carried out at 9.25 GHz using a standard reflection-type EPR spectrometer and a specially designed high-temperature cavity system in which the sample is heated by hot flowing N_2 gas, whereas the microwave cavity is kept at ambient temperature [14]. The samples were prepared starting from the appropriate amounts of oxides and carbonates by the usual ceramic processing involving repeated grinding and sintering. X-ray diffraction investigations using a Rigaku D/Max diffractometer showed the samples to be single-phase perovskites. The measurements of the static magnetic susceptibility χ_0 needed
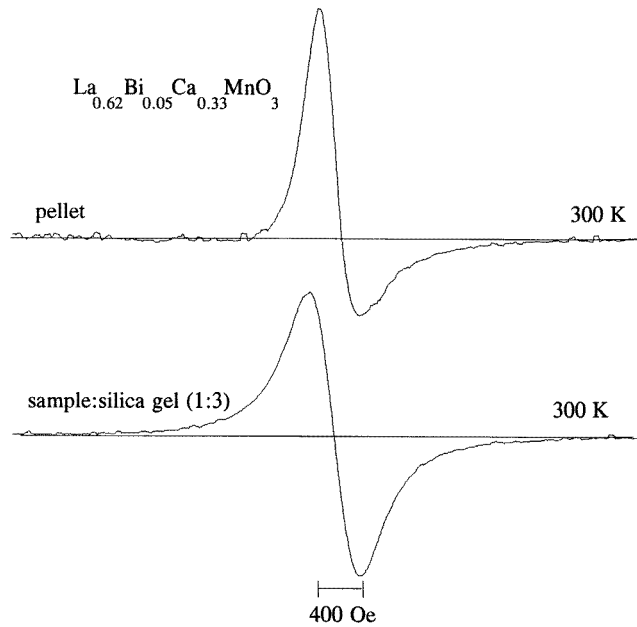
Figure 2. First-derivative EPR spectra for an undiluted sample and a diluted sample of $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$.

for the interpretation of the EPR data were done at 200 Oe using a SQUID magnetometer (Quantum Design Model MPMS). The temperature dependence of the electrical resistivity in applied fields of $H = 0$ and $H = 40$ kG was obtained using the standard four-probe technique and the SQUID magnetometer; the data for the $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ sample are shown in figure 1, showing a magnetoresistance of about 45% near T_c. Using the resistivity $\rho \simeq 0.3 \times 10^{-3}$ Ω cm at 300 K (figure 1), we estimate the skin depth $\delta \simeq 10$ μm at 9 GHz. So, unless the sample thickness is less than 10 μm, conductivity problems will lead to a dysonian lineshape. To eliminate both the sample size effect [13] and microwave conductivity problems, the samples for the EPR studies were powdered and diluted with EPR-inert silica gel. In figure 2, EPR first-derivative spectra for the undiluted (pellet) and the diluted $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ clearly show the dysonian lineshape for the undiluted sample and a symmetrical lineshape for the diluted sample. All of the remaining measurements reported here were done for the diluted samples and the linewidth ΔH refers to the peak-to-peak linewidth of the first-derivative spectra.

3. Experimental results

The temperature dependence of the static magnetic susceptibility χ_0 measured at 200 Oe is shown in figure 3 for both of the samples, giving $T_c = 238$ K for $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ and $T_c = 375$ K for $La_{0.67}Sr_{0.33}MnO_3$. Magnetoresistance studies of the former (figure 1) show that the peak in resistivity at $H = 0$ occurs slightly below T_c, a result known from the very early studies [6, 7]. The temperature dependence of the EPR linewidth for temperatures up to 700 K is shown in figure 4 for both the samples, diluted with silica gel in the ratio 1:3 (by weight) for $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ and 1:4 for $La_{0.67}Sr_{0.33}MnO_3$. For temperatures
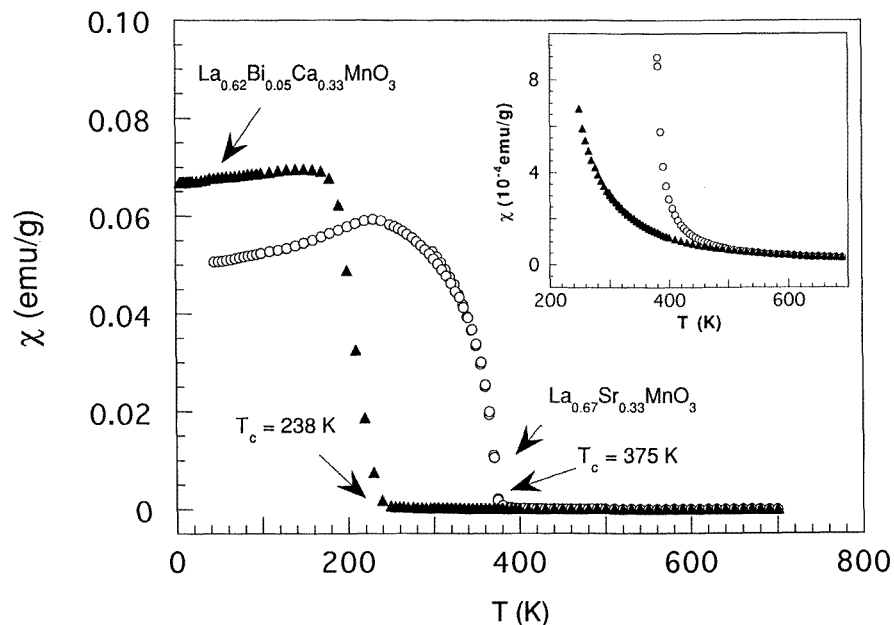
Figure 3. The temperature dependence of the static magnetic susceptibility for the two samples at 200 Oe. The inset shows the temperature dependence in the paramagnetic region.
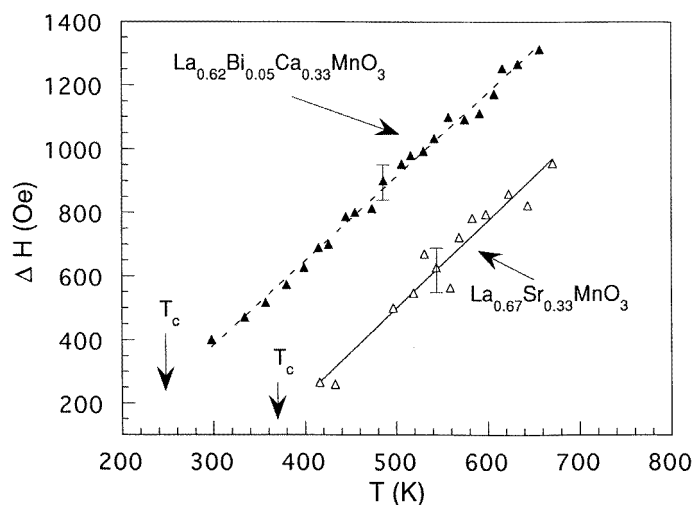

Figure 4. The temperature dependence of the EPR linewidth ΔH for the two samples. Lines are drawn through the points as a visual aid and the typical experimental uncertainty in ΔH is shown at one temperature.

above 700 K, the EPR signal became very weak and too broad for obtaining any meaningful data. As T_c is approached from above, the EPR lines become increasingly asymmetric and these data are not included in figure 4 because of the resulting uncertainties in ΔH. The results in figure 4 show that ΔH increases essentially linearly with temperature for both of

the samples for $T > T_c$. Also $g = 2.04 \pm 0.01$ for both of the samples and it is independent of temperature, although for $T > 500$ K, the g-value is difficult to measure accurately, because of the broadening of the line and weakness of the signal.

4. Discussion and interpretation

The temperature dependence of the EPR linewidths in ferromagnets and antiferromagnets for $T > T_c$ has been discussed in great detail in earlier papers by Castner and Seehra [15], Huber [16], Seehra and Huber [17] and Huber and Seehra [11]. First, it is noted that the mechanisms for the spin–lattice relaxation and associated EPR linewidths for a magnetic ion isolated in a non-magnetic host are very different [18] from those of concentrated magnetic systems where the various spin–spin interactions are the dominant cause for the observed EPR linewidths. For concentrated magnetic systems, the phonon modulation of the Heisenberg exchange interaction cannot produce a temperature-dependent EPR linewidth for $T \gg T_c$. This independent linewidth is observed in many S-state systems such as MnF_2, EuO, and $RbMnF_3$ [17], and certain $S = 1/2$ systems where antisymmetric exchange interaction is not the dominant anisotropy (see the review in reference [11]). The temperature-dependent EPR linewidths for $T \gg T_c$ can result from two sources: (1) the phonon modulation of the antisymmetric exchange interaction [15] as first observed and identified in $Cu(HCOO)_2 \cdot 4H_2O$ [19] and more recently in $CuGeO_3$ [20] and (ii) the phonon modulation of the crystalline field being the dominant mechanism for the relaxation of the magnetization as first proposed for the ferromagnet $CrBr_3$ [11] where a linear temperature dependence of the EPR linewidth is observed over an extended temperature range to 500 K, well above $T_c \simeq 32$ K [21]. This second mechanism is expected to be dominant for non-S-state systems with spin $S \geqslant 1$. For the manganates both Mn^{3+} ($S = 2$) and Mn^{4+} ($S = 3/2$) are non-S-state ions and, consequently, the situation is similar to that in $CrBr_3$ [11, 21] with $S = 3/2$ for Cr^{3+}, and a linear temperature dependence of the linewidth should be expected. As noted in reference [11], a broad band of phonons take part in the relaxation process, in contrast to the relaxation of an isolated magnetic ion where only narrow bands of phonons with energies comparable to the ionic level splittings are involved in one-phonon processes. This makes the one-phonon relaxation in the concentrated magnetic system far more effective than it is for an isolated magnetic ion. Also there should be no dependence of the EPR linewidth on the microwave frequency for $T \gg T_c$ as long as the resonance field $\ll$ the exchange field.

With the above background and discussion, it follows that the linear temperature dependence of ΔH observed here for the manganates is quite similar to that observed in $CrBr_3$ [21], a theory for which has been presented in reference [11]. Following the analysis in reference [11], the critical ($T \sim T_c$) and non-critical ($T \gg T_c$) contributions to ΔH can be separated (ignoring anisotropy in ΔH for polycrystalline samples) and ΔH can be written as [11]

$$\Delta H = \frac{\hbar[c + f(\varepsilon)]}{g\mu_B T \chi_0} \tag{1}$$

where μ_B is the Bohr magneton, $\hbar$ is Planck's constant, $f(\varepsilon)$ is the critical contribution to ΔH which is significant only for $\varepsilon = (T - T_c)/T_c \leqslant 0.1$, and c is the non-critical contribution from spin–spin and spin–phonon interactions for $T \gg T_c$. If there is no contribution to ΔH from spin–phonon coupling, then the product $\Delta H\, T \chi_0$ should become temperature independent for $T \gg T_c$.

To check the above analysis, plots of $\Delta H\, T \chi_0$ versus T are shown in figure 5 for
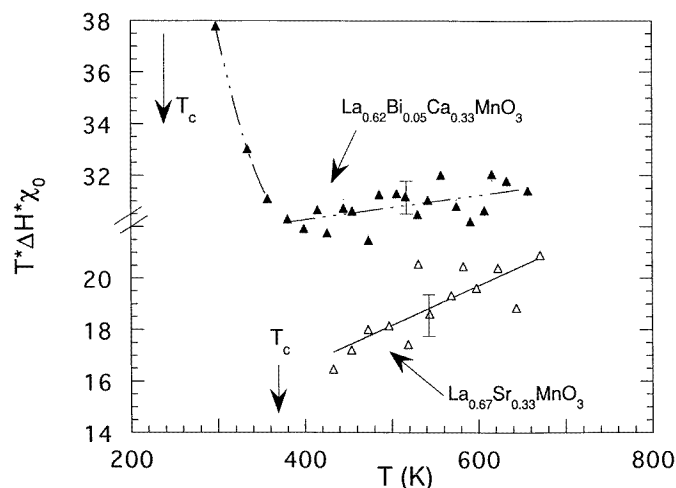
Figure 5. The temperature dependence of the product $\Delta H \chi_0 T$ for the two samples. Lines through the points are drawn for visual aid. The sharp increase in $\Delta H \chi_0 T$ at the lower temperatures is due to the onset of a critical contribution (see equation (1) and reference [11]).

both of the samples. Since the product $\Delta H \chi_0 T$ increases with temperature, albeit at different rates for the two samples, then following the above discussion, it is inferred that the observed temperature dependence is due to the spin–phonon coupling—somewhat similar to the observations in $CrBr_3$ [11, 12]. The spin–phonon contribution to ΔH may vary as T or T^2 depending on whether one-phonon or two-phonon contributions are dominant. Above, we have already noted why the one-phonon contribution can be so dominant in concentrated magnetic systems. To provide a more quantitative check on the magnitudes and anisotropy of the linewidths, EPR data on single crystals, detailed knowledge of the phonon spectra and magnitudes of various spin–spin interactions in the manganates are needed. This information is not available at present.

In summary, the experimental results on the EPR linewidths and their analysis for two doped manganates presented here have shown that spin–phonon interaction is the most likely cause for the observed linear temperature dependence of the EPR linewidth. These results support the view expressed in recent publications [8–10] that lattice effects play a significant role in the doped manganates with giant magnetoresistance.

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