Evidence for Competing Order Parameters in the Paramagnetic Phase of Layered Manganites

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Abstract:

The magnetic field and temperature dependence of the magnetic susceptibility and magnetization is studied for the ferromagnetic layered manganites $SrO(La_{1-x}Sr_xMnO_3)_2$ in the composition range $x = 0.32 - 0.40$. In the paramagnetic phase, the susceptibility exhibits an anomalous maximum at an intermediate magnetic field value. The size of this field-induced susceptibility enhancement increases dramatically with x from 10% for $x = 0.32$ to 160% for $x = 0.40$. The temperature dependence of the effect shows a maximum at $T \approx 1.1\ T_C$ for all x. Quantitative analysis in terms of the Landau theory of phase transitions enables us to identify a distortion of the free energy F in the paramagnetic phase that is associated with the susceptibility anomaly. This free energy distortion corresponds to a magnetic system that approaches a first order magnetic phase transition as the temperature is lowered towards T_C. Such a behavior is indicative of a second, competing order parameter, which is identified as the recently observed charge density wave. In the immediate vicinity of T_C, the anomaly disappears and the system seems to undergo a more conventional second order paramagnetic-ferromagnetic phase transition.

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I. Introduction

In recent years, there has been a renewed interest in doped manganese oxides, which has been triggered by the observation of the colossal magnetoresistance (CMR) effect in these materials [1]. The CMR effect is caused by the temperature dependent phase transition from a paramagnetic insulator to a ferromagnetic metal. Thus, for temperatures slightly above this phase transition an applied magnetic field does not only restore the magnetic order as it does in all types of ferromagnetic materials but also gives rise to metallic conductivity. The coincidence of the ferromagnetic-paramagnetic phase transition with the metal-insulator transition is generally believed to be associated with the double exchange mechanism [2-4]. Besides technological interest in the CMR effect, doped manganites are fascinating materials in that they exhibit a wide variety of unusual physical properties, which makes them considerably more complex than conventional transition metal ferromagnets [5]. While many of the early CMR studies were focused on perovskite manganites, there has been a surge of studies on layered manganite materials in the last few years. In particular the $n = 2$ variant of the Ruddlesden-Popper series $(La,Sr)_{n+1}Mn_nO_{3n+1}$ has interesting properties and is presently the focus of intense research efforts [6-27]. For instance, previous experimental studies reported an anomalous critical exponent β for the magnetization [17], charge density wave (CDW) type fluctuations [19], as well as antiferromagnetic (AF) correlations in the paramagnetic state [13,16-17]. Furthermore, specific heat measurements reveal an unusually large temperature dependent change in entropy in the paramagnetic phase [25]. All these anomalies, in connection with the disappearance of conductivity indicate a substantial change of the electronic state at the magnetic ordering temperature. These observations pose a fundamental question: *what happens to the magnetic exchange mechanism and the exchange coupling strength, if the electronic structure is so severely altered upon the ferromagnetic phase transition?* Surprisingly, one finds rather conventional critical behavior for the three dimensional (3D) $La_xSr_{1-x}MnO_3$ perovskites with almost perfect scaling properties, indicating that the ferromagnetic exchange mechanism is hardly influenced by the change in the electronic structure [28]. On the contrary, one would expect from a simple double exchange picture, that the ferromagnetic exchange breaks down once the conductivity disappears and hopping is suppressed.

In this paper, we investigate the above raised fundamental question of the ferromagnetic exchange coupling strength in the paramagnetic phase for the layered manganites $SrO(La_{1-x}Sr_xMnO_3)_2$ in the concentration range x = 0.32 – 0.40. Details on sample preparation and atomic structure have been previously published [10]. For the investigation of the microscopic structure, in particular the study of intergrowths, we have performed TEM measurements on ion-milled platelets. Magnetization and susceptibility (χ) measurements were made on both, a SQUID and an extraction magnetometer from Quantum Design, equipped with 7 and 9 T superconducting solenoids, respectively. Measurements were made with the applied field both parallel to the ab-plane (H ∥ ab) and parallel to the c-axis (H ∥ c). Resistivity measurements have been reported previously [20].

II. Experimental Results

Figure 1a shows the field-dependent ab-plane susceptibility χ(H) as a function of temperature in the paramagnetic phase for composition x = 0.36 in comparison to the expected susceptibility behavior of a conventional ferromagnetic system (Fig. 1b). From this comparison, one can identify two anomalies in the experimental data of the layered manganites that are not present in a simple ferromagnetic system. The first anomalous feature, which is observed in all the measurements shown in Fig. 1a, is the very sharp peak occuring at H ≈ 0. This peak is almost independent of temperature for the range shown here and it is caused by magnetic intergrowths defects, which are soft ferromagnetic entities up to their perovskite-like Curie temperature of approximately 300 K. Fig. 2a shows a more detailed low-field χ(H)-measurement for a x = 0.30 sample, which has an ordering temperature of 72 K [22]. In the vicinity of the ordering temperature, the low-field χ(H)-peak changes only weakly and even at T = 120 K a clear hysteresis effect is observed, which indicates the ferromagnetic nature of the low-field susceptibility anomaly. From the TEM-picture in Fig. 2b, it can be seen that intergrowths are stacking faults due to missing or extra layers of SrO between the MnO_6 octahedral planes. Such defects represent local inclusions of $n \neq 2$ variants of the Ruddlesden-Popper series. Especially n > 2 inclusions are expected to have a higher ordering temperature than the n = 2 host material and, therefore, cause a small soft-ferromagnetic

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background in the paramagnetic phase. Typical intergrowth concentrations are in the 0.1 – 1% range. Detailed studies of these defects have been published elsewhere [20, 23].

As one can see from Fig. 1b, the susceptibility in a conventional ferromagnet exhibits a more or less broad maximum at H = 0 in the paramagnetic state. The χ decrease for increasing field strength in due to the alignment of moments that cannot be further oriented once the magnetization saturates. For temperatures near T_C a small field is already sufficient to align a significant fraction of the moments and one observes a sharp drop of $\chi(H)$ upon increase of the field as shown by the experimental data for T = 130 K in Fig. 1a. For temperatures far above the Curie temperature, one needs much larger fields to induce a significant magnetization and observe saturation. This can readily be seen in the theoretical curve for T = 1.5 T_C as well as for T = 180 K in the experimental data, where we observe an extended plateau region before saturation sets in. So, in the vicinity of T_C as well as for fairly high temperatures, the layered manganites behave like conventional ferromagnets. However, we find an anomaly in an intermediate temperature region from T $\approx$ 135 K, i.e. just above T_C to about 160 K,. For these temperatures, there is an initial increase of χ with increasing magnetic field and we observe a maximum in $\chi(H)$ for |H| > 0. This anomaly also exhibits a clear chemical trend as shown in Fig. 3. From being only a small effect for x = 0.32 this $\chi(H)$-anomaly becomes the dominant feature for x = 0.40. It should also be mentioned that the anomaly as well as the entire $\chi(H)$-curve are independent from the direction of field change, i.e. do not exhibit any hysteresis behavior, which is demonstrated by the symmetric shape of all curves in Fig. 3.

To illustrate the chemical trend as well as the temperature dependence of the anomaly we define the enhancement factor S as the ratio of the maximum susceptibility value normalized to the extrapolated zero-field susceptibility for each temperature. This quantity is displayed in Fig. 4 as a function of temperature for the various sample compositions. S increases substantially with the doping level x, from a maximum value of 1.1 for x = 0.32 to almost 2.6 at x = 0.40. In all concentrations x, the temperature dependence of the effect is similar, showing a maximum at T $\approx$ 1.1 T_C. To better understand the origin of this anomaly we measured the magnetization dependent susceptibility $\chi(m)$. As an example Fig. 5a displays the results for x = 0.36. Note that the

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intergrowths contribution has been subtracted from the data. From Fig. 5a we see that $\chi(m)$ peaks at an approximately constant magnetization value, at least for intermediate temperatures, where the phenomenon is well established. Thus, the observed shift in the field position for the $\chi(H)$-peaks in Fig. 3 only corresponds to the varying fields necessary to achieve a certain magnetization value. Only for very high temperatures or temperatures very close to T_C, we find a reduction of the magnetization value at which the susceptibility maximum occurs in addition to a reduction in the peak height itself. We are able to mimic the basic features of the observed anomaly, if we assume that the exchange coupling constant J actually depends on the field-induced magnetization m. Fig. 5b displays a set of $\chi(m)$-curves, which have been calculated in mean field approximation (MFA) under the assumption that J increases with m as indicated on the right hand side of Fig. 5b. For $T = 1.1\ T_C$ we find pronounced $\chi(m)$-peaks at intermediate magnetization values, which decrease substantially for higher temperatures. Also, the theoretically predicted positions of the $\chi(m)$-maxima capture the experimental high-temperature behavior rather well. Only near T_C does the MFA J(m)-calculation fail, which is indicative of the significance of fluctuations in this very temperature range.

III. Discussion

The measurement of $\chi(m)$ permits the analysis of our data in terms of the Landau theory of phase transitions, which assumes that the free energy F can be described by a Taylor expansion in the order parameter, i.e. the magnetization m. Even though, this mean-field picture yields incorrect critical exponents, it allows a basic quantitative analysis of phase transitions, in particular a classification with respect to the order of the phase transition without invoking a specific microscopic model. We found it sufficient to fit a polynomial of sixth order to our experimental data, according to

$$F = \tfrac{1}{2}a \cdot m^2 + \tfrac{1}{4}b \cdot m^4 + \tfrac{1}{6}c \cdot m^6 - h \cdot m, \tag{1}$$

which corresponds to the following fitting-function for the magnetization dependent susceptibility

$$\chi(m) = \frac{1}{a + 3b \cdot m^2 + 5c \cdot m^4}. \tag{2}$$

For each temperature, we determine the coefficients a, b and c using a least-squares fit. The coefficient a corresponds to the inverse zero-field susceptibility and is required to be positive in the paramagnetic phase ($T > T_C$). c describes the saturation behavior at large fields and has to be positive as well. Thus, only a negative b is able to describe the observed susceptibility peak at intermediate magnetization values. Results for $x = 0.36$ are shown in Fig. 6. The curves for the other compositions are qualitatively the same. For temperatures above 150 K, a shows the conventional Curie-Weiss behavior and only in the vicinity of T_C are deviations visible. Even though one expects deviations from the Curie Weiss behavior near T_C, the effect observed here is unusual, because the data for a lie below the high temperature extrapolation, whereas conventional 2D or 3D systems would produce data lying above the extrapolated curve as indicated by the dashed line. This behavior has been explained by the dimensional crossover occurring in these weakly coupled manganite layers [24].

The susceptibility anomaly is described by a negative b factor, which is also displayed in Fig. 6. This parameter is not merely a quantitative description of the observed behavior, but rather a key quantity because it defines the order of the phase transition at T_C. For positive b values one observes the conventional second order phase transition, whereas negative b values indicate that the phase transition will be discontinuous [29]. It is this fundamental significance of b that makes the observed paramagnetic properties so very interesting, because the sign of b is actually changing right in the vicinity of T_C. At high temperatures, the system seems to be going towards a first-order ferromagnetic phase transition, whereas ultimately a second-order phase transition is observed.

In terms of the free energy F, the observed anomaly corresponds to a deformation of the conventional energy surface, in particular to an enhanced stabilization of the $m \approx 0$ state as shown schematically as an inset in Fig. 6. The conventional paramagnetic free energy function $F(m)$ is shown as a solid line and is compared to the behavior reported here for the layered manganites (dashed line). For small values of the magnetization the

anomalous state exhibits an unusually narrow minimum in F, which can be explained in two ways, namely either by a reduction of the magnetic moment per unit cell, or by lowering of the ferromagnetic exchange coupling J, which has already been discussed in connection with Fig. 5. It seems unlikely that the magnetic moment is changed, as such changes are typically associated with large energies. Thus, the anomalies suggest a substantially reduced J for the paramagnetic state. It, furthermore, seems that the full coupling strength can be restored by applying a sufficiently large field. At this point, the free energy of the anomalous state becomes equal to a conventional paramagnetic state, as indicated in Fig. 6. This interpretation in terms of a magnetization dependent exchange coupling is also consistent with the observed dramatic shift of T_C with applied field in these layered materials [15]. It should also be mentioned that even though J is significantly reduced in the paramagnetic state, it is still strongly ferromagnetic, as one can see from the inverse susceptibility, shown as factor a in Fig. 6.

The exchange constant reduction seems to be related to the charge density wave (CDW) formation, which was recently reported for x = 0.40 [19], because all experimental parameters are strongly correlated for both phenomena. The CDW appears only in the paramagnetic phase, shows a maximum in intensity at $T \approx 1.1 \, T_C$, and slowly disappears with increasing temperature. Furthermore, it can be suppressed by a sufficiently strong magnetic field, similar to the one we have found here to be necessary to restore the full exchange coupling. Thus, the paramagnetic phase has two distinct regions: (i) a CDW region with a reduced J for small applied field, and (ii) a high-field region, in which J is restored and the CDW disappears. The transition between these regions is broad and does not seem to be a true phase transition but rather a change in the fluctuation characteristic. So, the layered manganites exhibit a complex paramagnetic state, in which the ferromagnetic exchange competes not only with thermal fluctuations but also with the CDW as a second ordering mechanism. Such an interpretation of the CDW as a competing order mechanism is also in good agreement with the observed chemical trend, where we find an increasingly suppressed exchange coupling with increased doping level. One would expect such a doping dependence from a CDW-type mechanism as one moves closer to half-filling (x = 0.50). This competing interaction might also relate to the x dependence of T_C. In the layered manganites, T_C exhibits a

maximum at x = 0.36 which has been correlated with a sign-reversal in the MnO_6 octahedral distortion [18]. Upon increasing x one finds a substantial reduction of T_C, which is very different from the 3D $La_xSr_{1-x}MnO_3$ perovskites with the same doping level [30]. Thus, the occurrence of the CDW in the layered manganites might be responsible for the T_C reduction.

Another important observation is the fact that the position of the susceptibility maximum, as seen in Fig. 5, is changing towards smaller magnetization values near T_C, where strong ferromagnetic fluctuations are present. In addition, the peak-amplitude S is reduced upon approaching T_C. Therefore, the CDW is already suppressed if ferromagnetic fluctuations become strong and the system seems to undergo a second order phase transition. However, we are unable to observe conventional scaling behavior above T_C as shown in Fig. 7. Here, we have plotted magnetization vs. susceptibility curves that we measured on a x = 0.32 sample in the vicinity of T_C = 106.7 K. According to the scaling relations for a conventional second order ferromagnetic phase transition, $m(\chi)$ is given by

$$ln(m) = \frac{1}{1-\delta}ln(\chi) - \frac{1}{1-\delta}ln\left(\frac{1}{\delta}\cdot\left(\frac{T-T_C}{T_C}\right)^{-(\gamma+\beta(1-\delta))}\right) \qquad (3)$$

near the critical point with β, γ, and δ as the critical exponents [31]. Using a double logarithmic plot in Fig. 7, we expect the $m(\chi)$-data for the various temperatures to fall onto parallel lines as indicated by the dashed lines. The data do indeed show such behavior, but only in the ferromagnetic regime. For T > T_C the slope is not constant and changes even in the immediate vicinity of T_C. We therefore do not observe a universal scaling exponent δ in the paramagnetic phase, which is consistent with the fact that the character of the phase transition actually changes from second to first order in the immediate vicinity of the transition itself. Such a change in phase transition character results in a suppression or at least distortion of the critical region, in which scaling laws can be observed.

In summary, our study of field and temperature dependence of the susceptibility for $SrO(La_{1-x}Sr_xMnO_3)_2$ (x = 0.32 – 0.40) shows that the paramagnetic phase in these ferromagnetic layered manganites exhibits a reduced ferromagnetic exchange coupling, contrary to observations in chemically similar 3D perovskite materials. Thus, the change in the electronic structure at T_C reflects itself not only in the conductivity, as in all CMR-materials, but also in a substantial change of the FM exchange coupling. J is a key parameter of the electronic groundstate and it should be more accessible to a quantitative theoretical description than the non-equilibrium transport phenomena associated with the CMR-effect. The exchange constant reduction appears to be strongly correlated with the CDW-formation. The thermodynamic behavior of the paramagnetic state is highly anomalous, because it is driven by a competition between ferromagnetic and CDW fluctuations.

Figure Captions:

Figure 1: field-dependent susceptibility: (a) χ(H)-data for composition x = 0.36 as a function of temperature T > T_c; (b) χ(H)-behavior of a conventional ferromagnet. Both graphs are semi-logarithmic and cover a factor of 40 for the full-scale of the χ-axis.

Figure 2: (a) low field χ(H)-data for composition x = 0.30 in a wide temperature range between T = 20 K and T = 200 K; (b) high-resolution TEM micrograph showing the detailed structure of a n = 5 intergrowths (marked with a pointer),

Figure 3: field-dependent susceptibility χ(H)-data for compositions x = 0.32, 0.36, 0.38, and 0.40 as a function of temperature T > T_c. All graphs are semi-logarithmic and cover a factor of 40 for the full-scale of the χ-axis.

Figure 4: susceptibility enhancement-factor S vs. reduced temperature T/T_c for compositions x = 0.32, 0.36, 0.38, and 0.40.

Figure 5: susceptibility χ vs. magnetization m: (a) measurement for composition x = 0.36 as a function of temperature T > T_c. The thin solid lines connect the χ-peak positions for the individual curves; (b) mean field calculation for a magnetization dependent exchange coupling constant J(m) (scale on the right hand side).

Figure 6: Landau parameter a ($\bullet$) and b ($\bigcirc$) vs. temperature for composition x = 0.36. The solid line is a linear fit of the high temperature data of a; the dashed line indicates the conventional behavior of a for a 2D or 3D system near T_c. (Inset: schematic of the free energy F vs. magnetization (M/M$_S$) for the paramagnetic state. The solid line illustrates the behavior of a

conventional ferromagnet, whereas the dashed line corresponds to the distorted energy surface observed here.)

Figure 7:   magnetization vs. susceptibility data measured for a x = 0.32 sample in the vicinity of T_c = 106.7 K; the dashed lines indicate the expected scaling behavior for a conventional ferromagnet; the solid lines are a guide to the eye, connecting the low-field data for each individual temperature.

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Figure 1

(a)

ab-plane susceptibility

T = 20 K

T = 40 K

T = 60 K

T = 80 K

T = 100 K

T = 120 K

T = 200 K

-200   0   200

mag. field (Oe)

(b)

20 Å
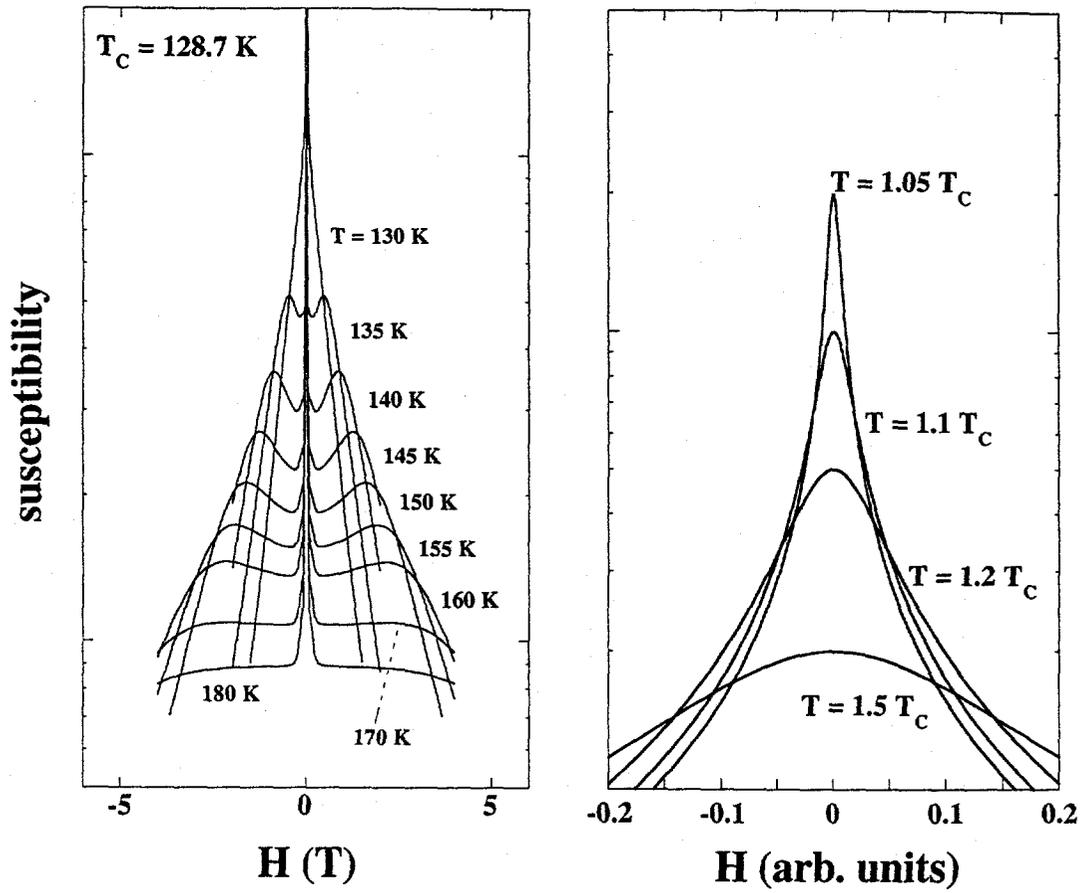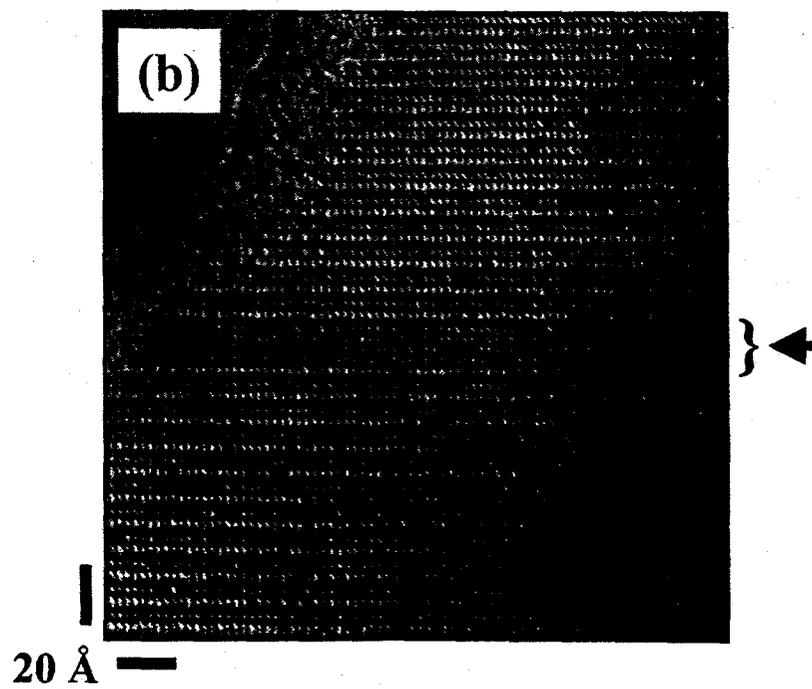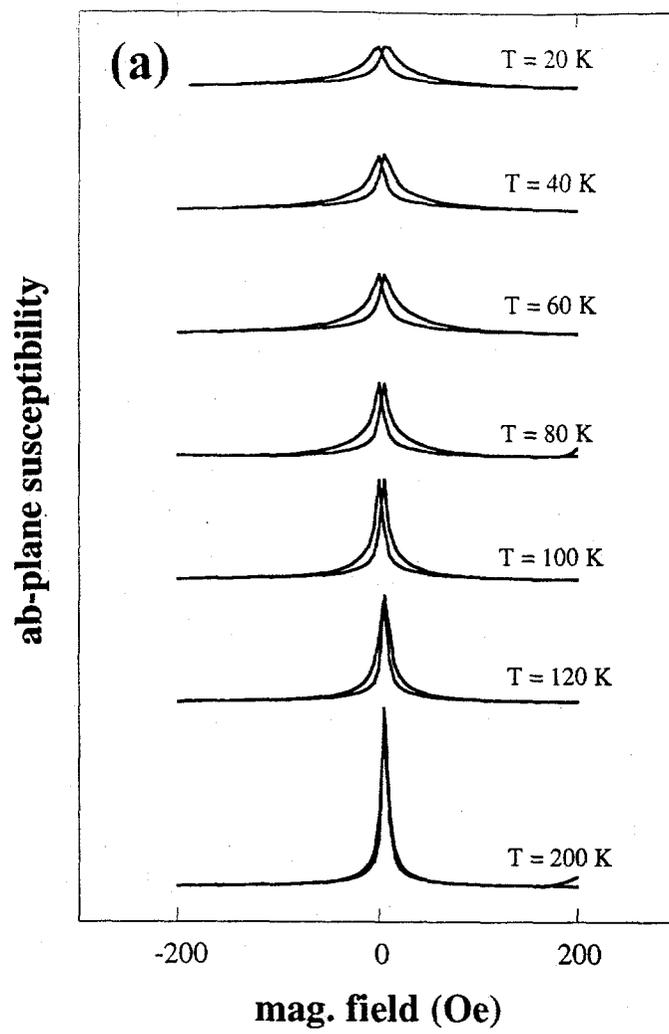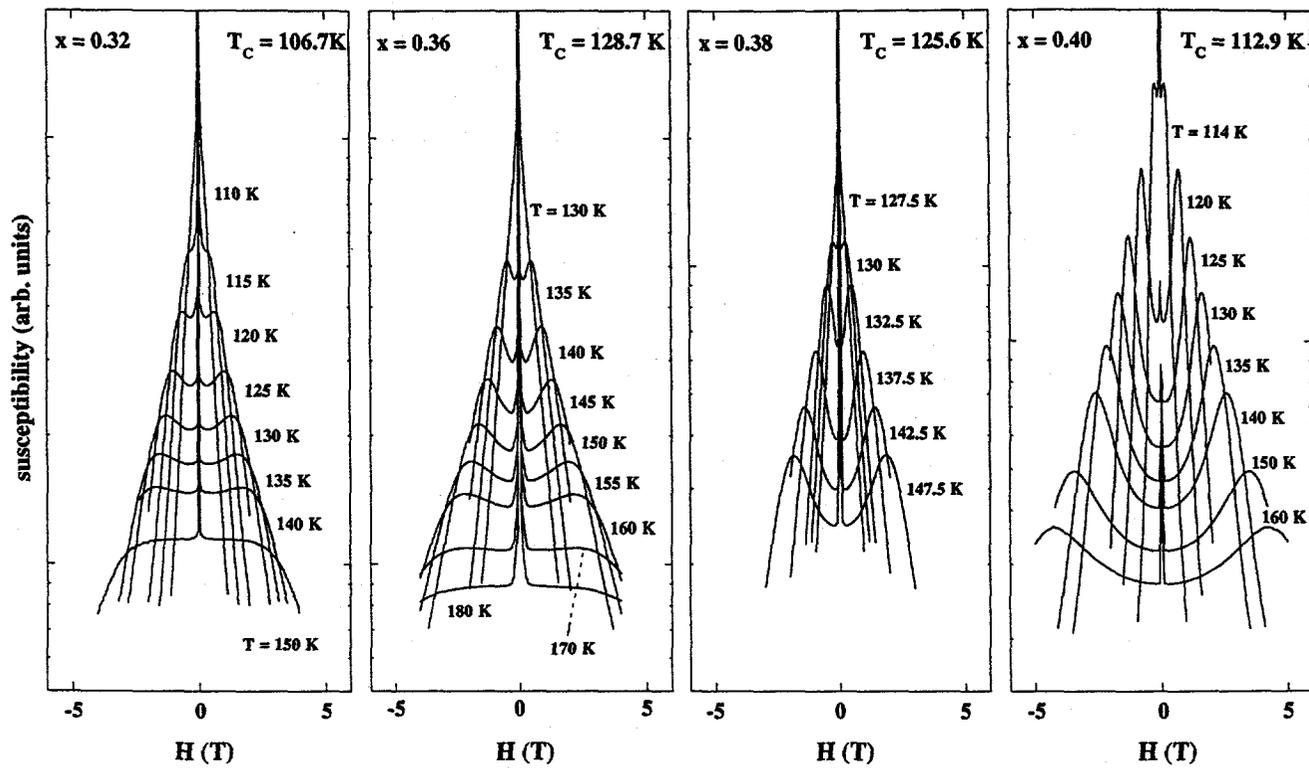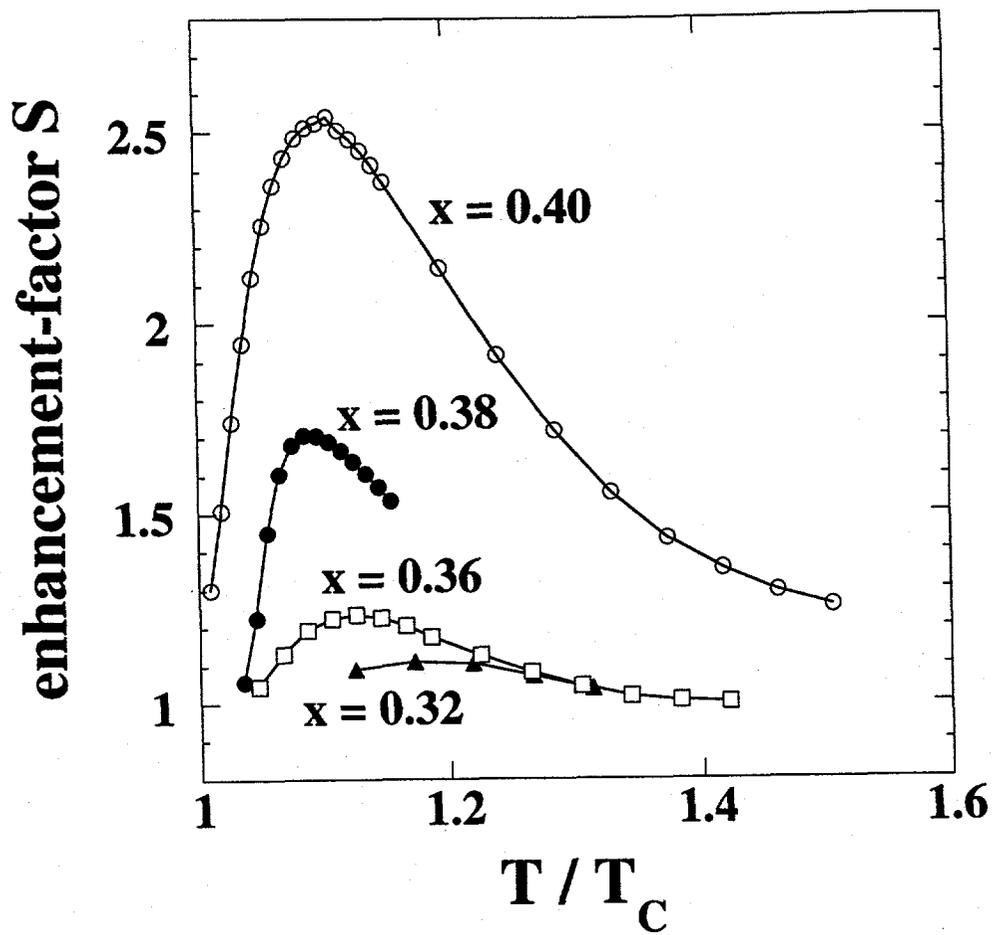
Figure 2

Figure 3

Figure 4
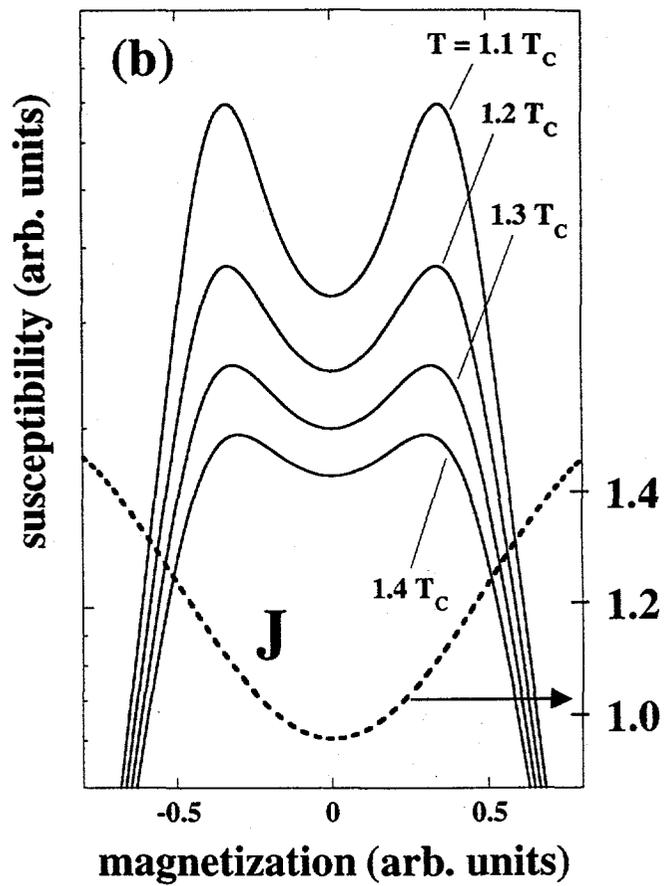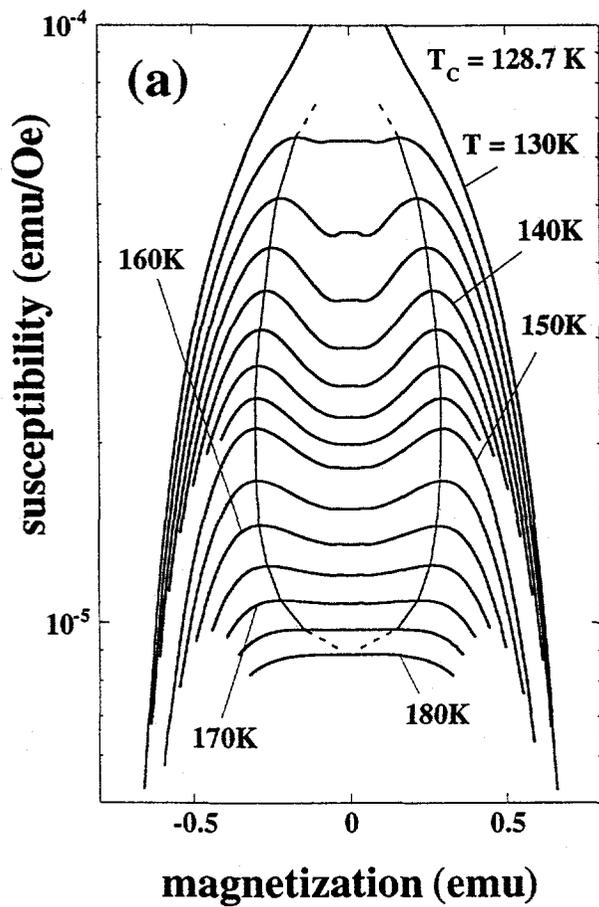
Figure 5

Figure 6

Figure 7