Role of Double Exchange in the Magnetic Structure of $Li_xMn_{1-x}Se$†

R. R. HEIKES
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania*

AND

T. R. MCGUIRE AND R. J. HAPPEL, JR.
U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland

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The details of the magnetic behavior of the $Li_xMn_{1-x}Se$ system are attributed to the double-exchange interaction. At low temperatures, the hole which is introduced by the Li^+ is loosely bound to the Li^+ itself. In the region of the Li ion, double exchange causes local distortions of the spin system which we refer to as clusters. As the Li concentration is increased ($x=0.07$), the clusters overlap sufficiently so that a magnetic field will induce an appreciable magnetic moment ($0.5\,\mu_B$). At temperatures below 45°K a canted spin ordering is suggested as the magnetic model for the $x=0.07$ composition. Finally, at $x=0.10$ we find that spontaneous magnetization develops below 110°K. As the temperature is lowered through 70°K the spontaneous moment disappears and antiferromagnetism is found. It is not inconsistent with the data for $x=0.10$ that this antiferromagnetic state is a canted-spin system with very small canting angle and therefore small magnetic moment. The theory of de Gennes is used in our discussion of the magnetic model.

I. INTRODUCTION

THE possibility that a ferromagnetic coupling might arise from the inherent degeneracy found in a crystal possessing an ion in two different valence states was first proposed by Zener.[1] This interaction, termed double exchange, which also gives rise to a metallic-type conductivity, was introduced to explain the ferromagnetic and electrical properties of certain perovskite systems.[2] To gain further insight into this type of interaction, Johnston and Heikes[3,4] studied several Li-substituted transition metal oxides. As the substitution of monovalent lithium introduces mixed valence states in the metal ion lattice, it was anticipated that ferromagnetism would be induced in certain composition ranges; however, no ferromagnetism was found. Furthermore, all the compounds studied were semiconducting[4] rather than metallic. The absence of metallic conduction led to the belief that the double-exchange interaction is pre-empted when the charge carriers are trapped at lattice sites due to the induced polarization of the surrounding lattice produced by the charge carrier itself. Under these conditions the possible degeneracy has only a negligible effect on the state of the electron. Rather, the electron can be treated classically and its motion can be considered as a thermally activated diffusion process.

As the strength of the electron trapping was known[5] to vary inversely with the electronic polarization of the lattice, it was conjectured that the replacement of oxygen by selenium in $Li_xMn_{1-x}O$ might produce the desired ferromagnetism. From initial magnetic studies[6] of this system (carried down only to 77°K) it appeared that ferromagnetism was present in the composition range $0.05 \lesssim x \lesssim 0.11$.

The present investigation of the magnetic properties, done in conjunction with a neutron diffraction study by Pickart, Nathans, and Shirane,[7] has revealed that the system is not nearly so simple as anticipated. However, it is quite clear that double-exchange effects are predominant in this system.

II. EXPERIMENTAL RESULTS

The preparation of the $Li_xMn_{1-x}Se$ system cannot be extended beyond $x=0.11$ because additional phases appear. Below this composition the materials are single phase with the NaCl structure.

Studies of electrical resistance and Seebeck coefficients made by Miller[8] indicate that each composition has a resistance minimum at temperatures between 80 and 130°K. As the lithium concentration increases, the temperature at which this minimum occurs decreases. Above the minimum there is the typical increase of resistance common to metallic type conduction. At low temperatures the resistance again increases, indicating that some of the current carriers are being trapped in the region of a Li ion.

Magnetic moment and magnetic susceptibility measurements were made from 4°K to 800°K. In both cases a force method was used. The magnetic susceptibility apparatus is a small torsion balance in an enclosed system,[9] while the magnetic moment balance is one

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* This work has been partially supported by the Navy Department Bureau of Ships.

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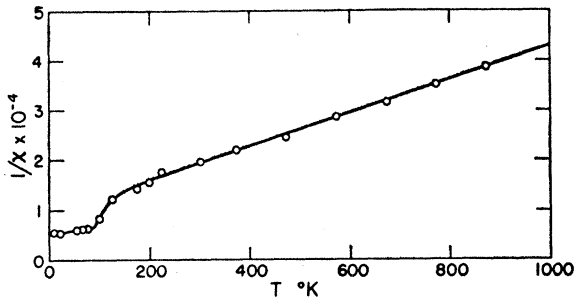

FIG. 1. Reciprocal magnetic susceptibility (x in units of emu/gm) vs temperature for $Li_{0.03}Mn_{0.97}Se$.

designed by Maxwell and Pickart.[10] A detailed description of the apparatus and experimental techniques used in these measurements will be found in sections written, respectively, by McGuire and Maxwell.[11]

MnSe

Although no measurements were made by us on this material, its characteristics are important as the starting point of the system. MnSe is known to be antiferromagnetic and magnetic susceptibility (χ) measurements have been made by several investigators.[12–14] Lindsay[14] found a temperature hysteresis of the magnetic susceptibility which he attributed to a crystallographic phase change. X-ray studies by Taylor[15] indicate that two phases are indeed present below 143°K, a NiAs phase appearing. The Néel temperature from susceptibility data is found at about 130°K when going down in temperature but on warming it is apparently considerably higher. According to neutron diffraction measurements of Shull, Strauser, and Wollan[16] MnSe has a spin ordering of the second kind similar to MnO.

$Li_{0.03}Mn_{0.97}Se$

The magnetic susceptibility measurements of this material are shown in Fig. 1. Over the temperature range studied the susceptibility is independent of magnetic field within a few percent. At temperatures below 200°K the $1/\chi$ curve has a pronounced departure from linearity. There is a sharp break in the region of 90°K. At still lower temperatures, χ becomes almost constant in value.

$Li_{0.05}Mn_{0.95}Se$

The data are illustrated in Fig. 2. Features similar to the $x=0.03$ sample are present except that now the susceptibility is field dependent at temperatures below 83°K. The magnetic moment per Mn atom versus temperature is also shown in Fig. 2. For an applied field of 6480 oersteds a value of 0.15 μ_B is measured but saturation has not occurred at this field strength.

$Li_{0.07}Mn_{0.93}Se$

At this composition a ferromagnetic moment appears (Fig. 3). Figures 4 and 5 show magnetization curves for temperatures of 77°K and 20°K. At 77°K there is an induced moment but no remanent magnetic moment; however, remanence is found at 20°K. The magnetic moment at 20°K could be due to ferrimagnetism caused by ordering of Li ions. This idea was tested by measurements on heat treated samples. A specimen held at 600°C for several hours and then quenched in water gave a moment of 0.6 μ_B at 20°K while a sample slow-cooled 1°C/min from 600° dropped to 0.4 μ_B. Although no explanation of this decrease in moment is offered, it is contradictory to what is expected of ordering phenomena, for in this case the slow-cooled sample, being better ordered, should have a higher moment.

$Li_{0.10}Mn_{0.90}Se$

Figure 6 shows the behavior of this composition. The Curie temperature is at approximately 110°K while at 70°K there is a sharp drop in the magnetic moment to a very small value. At the lower temperature a thermal hysteresis is present. This temperature is evidently a Néel point, first found by neutron diffraction as discussed in the following paper. The magnetic susceptibility below 70°K has a field dependence which is opposite to that of a standard antiferromagnetic substance, that is, χ decreases with increasing field such as observed when a small ferromagnetic impurity is present.

Figure 7 shows the magnetization curves with increasing field strength at 77°K for each sample investigated.

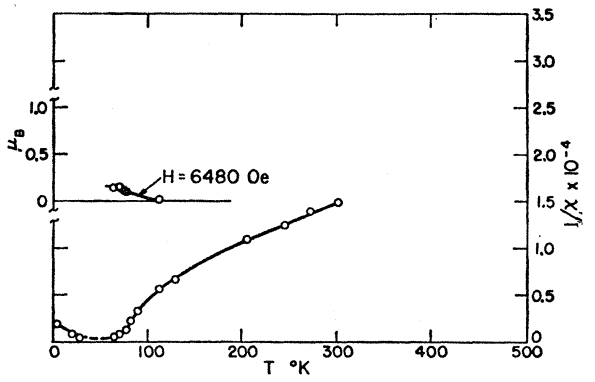

FIG. 2. Reciprocal magnetic susceptibility (x in units of emu/gm) and average magnetic moment (in Bohr magnetons) per Mn atom vs temperature for $Li_{0.05}Mn_{0.95}Se$.

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[16] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. **83**, 333 (1951).

TABLE I. Magnetic parameters obtained from susceptibility data for $Li_xMn_{1-x}Se$.

x	$C_M\left(\frac{\text{emu °K}}{\text{mole}}\right)$	θ (°K)	μ_{eff} (μ_B)	μ_{eff}[a] (μ_B)
0.03	3.96	−250	5.65	5.56
0.05	3.19	− 53	5.08	5.33
0.07	3.20	− 24	5.08	5.11
0.10	2.80	+ 55	4.76	4.79

[a] Calculated on the assumption that $Mn^{+++}=0\ \mu_B$.

Table I gives values of C_M, the molar Curie constant from which the effective magnetic moment (μ_{eff}) is calculated. In all cases the values of μ_{eff} are lower than would be expected for $(1-2x)Mn^{++}$ and xMn^{+++} if we assume five electron spins for Mn^{++} and four unpaired electron spins for Mn^{+++}. The decrease corresponds within 1% to $xMn^{+++}=0\ \mu_B$ with the possible exception of composition $x=0.05$. In this case the measurement went only to 300°C and this is probably not high enough to determine an accurate C_M. The zero μ_{eff} value for Mn^{+++} was also found for $Li_xMn_{1-x}O$.[3] This zero moment presumably arises because the ground state of Mn^{+++} has $J=0$, that is, L and S are equal and opposite. It is, however, difficult to understand why excited states having nonzero values of J are not detected.

The third column of the table, headed θ, is the intercept on the temperature axis of the high-temperature slope of $1/\chi$ from which C_M was calculated. According to the analysis of double exchange by Anderson and Hasegawa[17] the shape of this curve is hyperbolic and the asymptote should intercept at 0°K. However, de Gennes[18] has shown that the exact form of the $1/\chi$ vs T curve depends on the width of the energy bands with respect to kT and this could account for the variation found for θ. Further, in the present system there are two complications: (1) antiferromagnetic interactions are present; (2) additional effects are caused by the precipitation of the charge carriers. It is therefore not surprising that θ is unequal to zero.

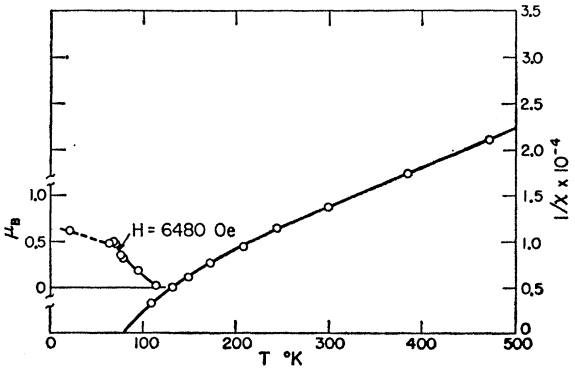

FIG. 3. Reciprocal magnetic susceptibility (x in units of emu/gm) and average magnetic moment (in Bohr magnetons) per Mn atom vs temperature for $Li_{0.07}Mn_{0.93}Se$.

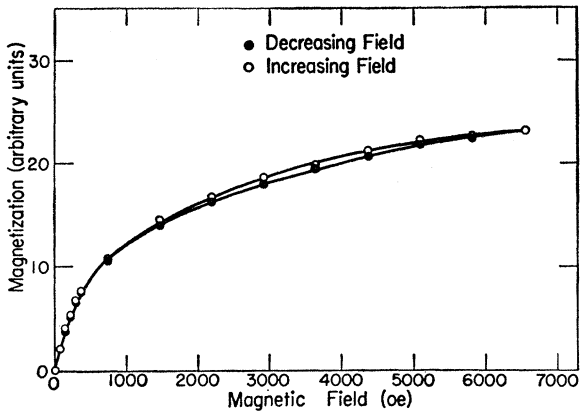

FIG. 4. Magnetization (arbitrary units) vs magnetic field at 77°K for $Li_{0.07}Mn_{0.93}Se$.

III. DISCUSSION OF RESULTS

The recent paper of de Gennes[18] has added considerably to the knowledge of the effects caused by double exchange. The results of his paper are summarized as:

(a) At sufficiently low temperatures a mixed-valence system, whose carriers are not trapped by the lattice polarization, will usually adopt a configuration such that the moments of the various sublattices are canted to one another.

(b) As the temperature is raised, the canted arrangement will give way to either a ferromagnetic or antiferromagnetic order depending on the magnitudes of the various interactions.

(c) If the charge carriers are trapped around impurity sites, they cause local spin distortions or inhomogeneities which in turn give rise to net local moments. At high temperatures and/or low concentrations these local moments behave as paramagnetic entities, that is, they are uncoupled. At low temperatures and/or high concentrations these entities may couple to give effects similar to (a) and (b).

(d) The form of the $1/\chi$ vs T hyperbolic curve predicted by Anderson and Hasegawa[17] is only correct if the bandwidth of the carriers is narrow compared to kT. If the opposite is the case, the ferromagnetic and extrapolated paramagnetic Curie temperatures agree.

It will be seen that the magnetic properties of $Li_xMn_{1-x}Se$ can be, at least qualitatively, understood on the basis of the double-exchange coupling outlined above.

$Li_{0.03}Mn_{0.97}Se$

The reciprocal-susceptibility curve for this composition (Fig. 1) shows a pronounced decrease at ~100°K. Studies of electrical resistivity and Seebeck coefficient[8]

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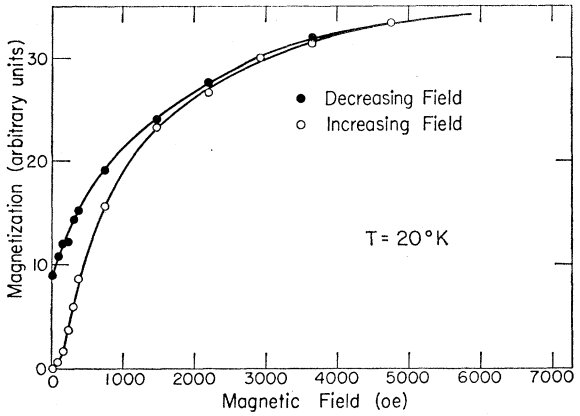

FIG. 5. Magnetization (arbitrary units) vs magnetic field at 20°K for $Li_{0.07}Mn_{0.93}Se$. Curve with open circles represents sample starting in demagnetized state and is not part of hysteresis loop.

of $Li_{0.03}Mn_{0.97}Se$ indicate that the current carriers are beginning to freeze out in the neighborhood of 130°K, that is, the Mn^{+++} ions become neighbors to a Li^{+}.

Since the 12 nearest neighbors of the Li are equivalent, these ions will be coupled by the charge carrier on the Mn^{+++}. As de Gennes has shown (c), under these conditions the double-exchange coupling will give rise to a local net moment. It is expected that these localized moments will behave paramagnetically and contribute the observed anomalous increases in χ found just above the Néel temperature. Below the Néel point the local moments, due to exchange coupling with the host lattice, will be constrained as part of the antiferromagnetic structure of the crystal. Because we are measuring powder materials no anisotropy effects are noticed. The relative constancy of χ below T_N is felt to be an accidental contribution of the local moments.

It should be pointed out that at these dilute concentrations where interactions between clusters are negligible a field dependence will not arise from these moments even below the antiferromagnetic Néel temperature. The moment is simply proportional to the field.

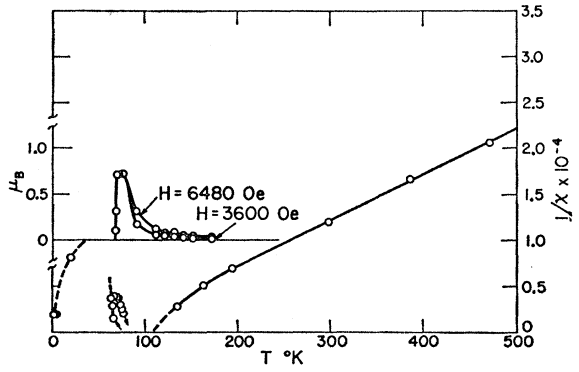

FIG. 6. Reciprocal magnetic susceptibility (x in units of emu/gm) and average magnetic moment (in Bohr magnetons) per Mn atom vs temperature for $Li_{0.10}Mn_{0.90}Se$. Arrow pointed up indicates measurements as temperature is lowered while arrow pointed down is for measurements taken as temperature is increased.

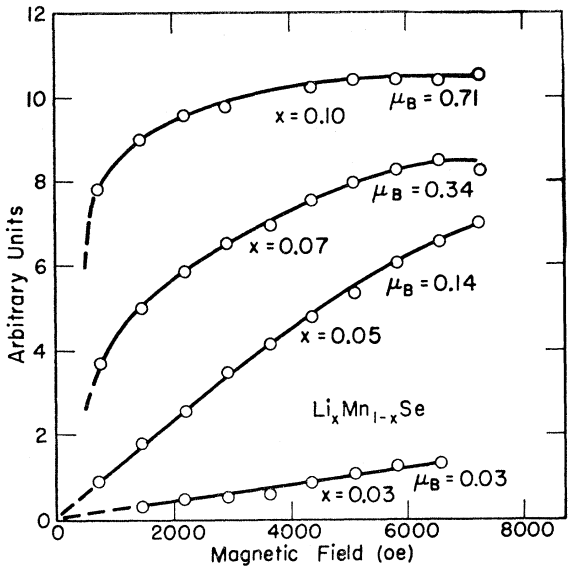

FIG. 7. Magnetization (arbitrary units) vs magnetic field at 77°K for $Li_xMn_{1-x}Se$. The magnetic moment (in Bohr magnetons per Mn atom) listed below each curve is the value at the field measurement, 6480 oersteds.

$Li_{0.05}Mn_{0.95}Se$

Due to the increased Li concentration the double-exchange interaction is more prominent. The $1/\chi$ vs T decreases rapidly at 83°K indicating a magnetic transition. Below this temperature there is a field-dependence of the susceptibility; for example, in Fig. 7 it is seen that saturation effects are just showing up at the highest fields. The magnetic clusters are now sufficiently close together so as to interact with one another slightly, thus causing the above effects. The neutron diffraction results show that antiferromagnetism occurs below 83°K. Since the diffraction lines are unaffected by a magnetic field at 64°K, the clusters are still coupled to the antiferromagnetic lattice and any realignment caused by the magnetic field is only through a relatively small angle. This is consistent with the magnetic measurements since the magnitude of the moments is less than 0.2 μ_B per Mn atom.

$Li_{0.07}Mn_{0.93}Se$

Below 100°K the magnetization curves (Figs. 4 and 5) show an induced moment at 77°K while at 20°K a true spontaneous moment exists. That this is not ferrimagnetism is understood from the saturation measurements on quenched and slow-cooled samples which reveal no evidence of ordering phenomena.

The interpretation of the magnetic data must be considered closely with the neutron diffraction results which show the region below 100°K to be antiferromagnetic. At 64°K certain diffraction lines are sensitive to the presence of a magnetic field (in contrast to the $x=0.05$ sample). Finally, at 45°K the neutron data indicate a change in spin axis.

We again assume the existence of magnetic clusters surrounding Li ions due to the freezing out of charge

carriers. The increased amount of Li and consequent increased number and proximity of the clusters results in stronger interactions between them. This in turn helps to overcome antiferromagnetic exchange interactions. The clusters may now be easily rotated by a magnetic field giving magnetization curves typical of Fig. 4 and this same effect would cause the antiferromagnetic scattering amplitude to be reduced. The behavior is similar to the 0.05 Li sample, except now the induced magnetic moment is larger and detected by both magnetic measurements and neutron diffraction techniques.

At 45°K the change in spin axis is interpreted as the formation of a canted system. This results in a nonzero spontaneous moment in low magnetic fields as shown in Fig. 5.

$Li_{0.10}Mn_{0.90}Se$

The Li concentration is now high enough so that the double-exchange interaction is dominant throughout the entire lattice rather than in isolated clusters. We observe a transition[19] at 70°K from ferromagnetism to antiferromagnetism with ordering of the third kind. This is confirmed by both neutron and magnetic data. The transition to ordering of the third kind is in accord with the fact that the next nearest neighbor antiferromagnetic coupling is weakened by the presence of the double exchange. From the work of de Gennes, however, we must look closely to see if the transformation is from a ferromagnetic lattice to a canted one rather than purely antiferromagnetic. This can certainly be true if the canted moment is very small. The small magnetic moment associated with the ferromagnetic-type field dependence of χ at temperatures below 70°K supports this hypothesis. Furthermore, the neutron diffraction would not detect a moment or canting angle of this small a magnitude.

The final answer on the exact low-temperature spin structure of $Li_{0.1}Mn_{0.9}Se$, and also the $Li_{0.07}Mn_{0.93}Se$ composition, will probably require single-crystal neutron diffraction investigation.

[19] It is not known at this time how closely the transition in $Mn_{0.9}Li_{0.1}Se$ compares with the transition recently reported in $Mn_{2-x}Cr_xSb$ [T. J. Swoboda *et al.*, Phys. Rev. Letters 4, 509 (1960)]. It is pointed out that the phase existing above the transition in the first material is ferromagnetic while the phase in the latter material is ferrimagnetic.

ACKNOWLEDGMENTS

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Magnetic Structure Transitions in $Li_xMn_{1-x}Se$†

S. J. PICKART
U. S. Naval Ordnance Laboratory, White Oak, Silver Spring, Maryland, and Brookhaven National Laboratory, Upton, New York

R. NATHANS
Pennsylvania State University, University Park, Pennsylvania, and Brookhaven National Laboratory, Upton, New York

AND

G. SHIRANE
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

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The magnetic structures occurring in lithium-substituted manganese selenide ($Li_xMn_{1-x}Se$) have been examined by low-temperature powder neutron diffraction measurements. The composition with $x=0.05$ retains the fcc ordering of the second kind found in MnSe, the transition temperature being lowered to 83°K. For $x=0.07$ the same type of ordering sets in at 73°K, but the spin direction changes abruptly as the temperature is lowered through 45°K; furthermore, the superlattice intensities decrease when an external magnetic field is applied along the scattering vector. At $x=0.10$, the spontaneous moment observed at 77°K by magnetization measurements is shown to be ferromagnetic, again by means of an external field, and a transition is found at 71°K from ferromagnetism to antiferromagnetism with the third kind of ordering. The results are discussed with relation to models containing canted spins and multiple antiferromagnetic axes.

I. INTRODUCTION

IN a magnetically ordered solid the orientation of the spins relative to one another is determined by exchange forces, and their direction relative to the crystalline axes by other (usually weaker) forces, such as magnetic dipolar interactions. While transitions involving a change of spin axis with temperature are well established,[1] attempts to verify suspected structure

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[1] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. 83, 333 (1951).