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

We wish to acknowledge the work of Dr. W. D. Johnston in preparing the samples and the many discussions which the authors have had with Dr. S. J. Pickart, Dr. Gen Shirane, and Dr. R. Nathans who carried out the neutron diffraction measurements.

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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

† Supported in part by the National Security Agency under the auspices of the U. S. Atomic Energy Commission.

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

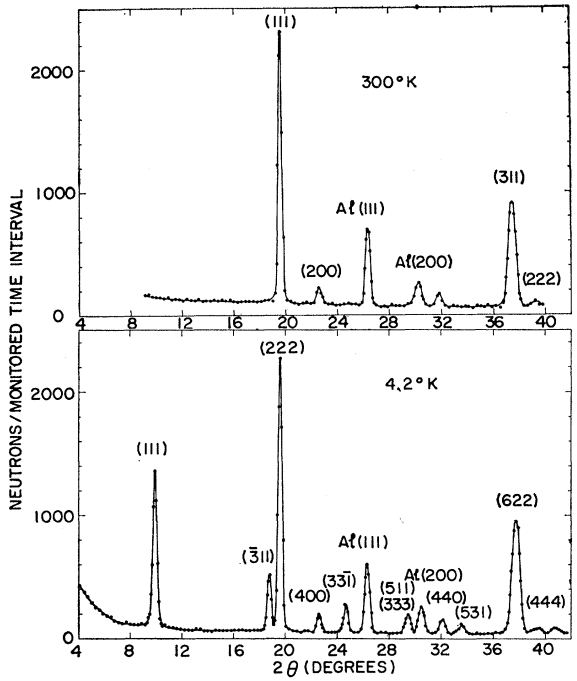

FIG. 1. Neutron diffraction patterns of $Li_{0.05}Mn_{0.95}Se$ at room temperature and 4.2°K.

transitions from one type of ordering to another[2–4] have had no simple interpretation. The present study reports neutron diffraction measurements on the mixed crystal system $Li_xMn_{1-x}Se(0\leqslant x\leqslant 0.11)$, which exhibits both kinds of transition, an anisotropy transition at $x=0.07$ and a ferromagnetic-antiferromagnetic phase change[5] at $x=0.10$. Complementary magnetization measurements are described in the accompanying paper by Heikes, McGuire, and Happel.[6]

MnSe in its stable form has the rock salt structure, with the metal atoms forming a face-centered cubic lattice. It is known to become antiferromagnetic but its Néel temperature is uncertain because of a thermal hysteresis, observed in both the susceptibility[7] and paramagnetic resonance,[8] which has been attributed by Lindsay[7] to the occurrence of crystallographic phase changes. However, the Néel point probably does not lie below 110°K.[8] The antiferromagnetic structure was reported by Shull, Strauser, and Wollan[1] to be fcc ordering of the second kind,[9] in which the spins alternate in sign along each cube edge, imparting a rhombohedral symmetry to the magnetic lattice. The spin axis was not explicitly mentioned, but if it is the same as in MnO, it is perpendicular to the unique [111] direction defined by the ordering.[10]

In order to determine whether the positive double-exchange interaction[11] could be made to operate in a rock salt type of compound, Johnston and Heikes[12] substituted monovalent lithium into various transition metal oxides, thus causing the magnetic cation to exist in two valence states. They ascribed the apparent non-occurrence of double exchange to local lattice distortions around the trivalent ion, and suggested that introduction of an anion with higher polarizability would relieve the distortions. Subsequently, they reported that the

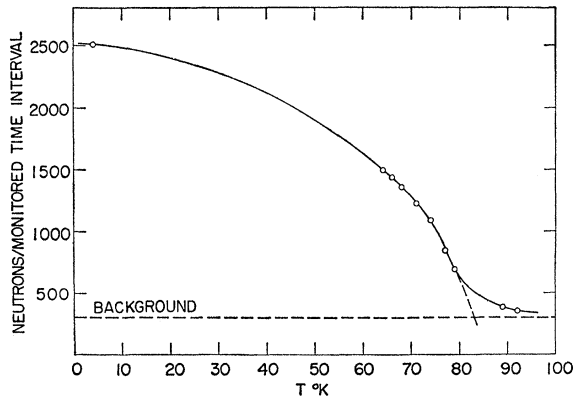

FIG. 2. Temperature dependence of the intensity of the (111) superlattice reflection in $Li_{0.05}Mn_{0.95}Se$.

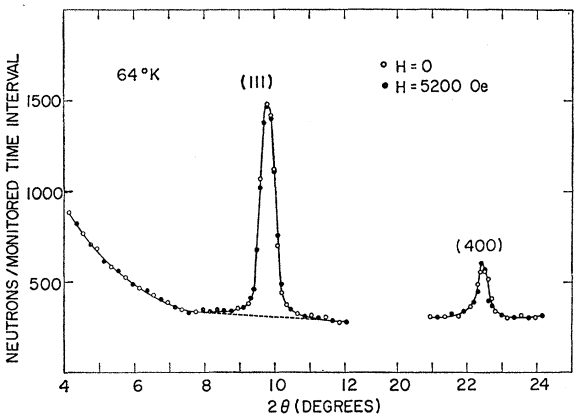

FIG. 3. Low-angle portion of the diffraction pattern of $Li_{0.05}Mn_{0.95}Se$ with and without a magnetic field applied parallel to the scattering vector.

[2] W. C. Koehler and E. O. Wollan, Phys. Rev. **97**, 1177 (1955).
[3] B. W. Roberts, Proceedings of the Conference on Magnetism and Magnetic Materials, Boston, 1956 (American Institute of Electrical Engineers, New York, 1957), p. 225.
[4] S. J. Pickart and R. Nathans, J. Appl. Phys. **30**, 280*S*, (1959).
[5] A brief report of this result has been given in Bull. Am. Phys. Soc. **4**, 52 (1959).
[6] R. R. Heikes, T. R. McGuire, and R. Happel, preceding paper [Phys. Rev. **120**, 703 (1961)].
[7] R. Lindsay, Phys. Rev. **84**, 569 (1959).
[8] L. R. Maxwell and T. R. McGuire, Revs. Modern Phys. **25**, 279 (1953).
[9] P. W. Anderson, Phys. Rev. **79**, 705 (1950).
[10] W. L. Roth, Phys. Rev. **110**, 1333 (1958); **111**, 772 (1958).
[11] C. Zener, Phys. Rev. **82**, 403 (1951).
[12] W. D. Johnston and R. R. Heikes, J. Am. Chem. Soc. **78**, 3255 (1956); W. D. Johnston, R. R. Heikes, and D. Sestrich, J. Phys. Chem. Solids **1**, 1 (1958).

replacement of one manganese atom in ten by lithium in MnSe did indeed result in a ferromagnetic moment.[13]

These neutron diffraction measurements represent an effort to learn in detail how the passage from an antiferromagnetic to a ferromagnetic spin lattice is accomplished. Three compositions of the $Li_xMn_{1-x}Se$ system (with $x=0.05$, 0.07, and 0.10) were examined at temperatures from 300° to 4.2°K and in applied fields up to 6800 oe. The diffractometer with its associated magnet and cryostat has been previously described.[14]

II. EXPERIMENTAL RESULTS AND ANALYSIS

$Li_{0.05}Mn_{0.95}Se$

The diffraction patterns obtained from the five percent composition at 300° and 4.2°K are illustrated in Fig. 1. The superlattice reflections appearing at 4.2°K can be indexed on a cubic cell with a lattice parameter twice that of the chemical cell, and are characteristic

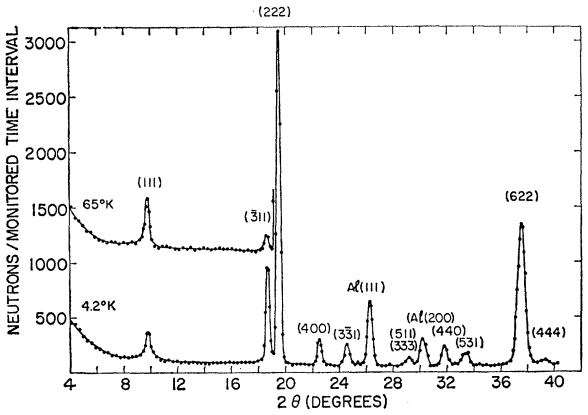

FIG. 4. Neutron patterns of $Li_{0.07}Mn_{0.93}Se$ at 65°K (low-angle portion) and 4.2°K.

of the second kind of fcc antiferromagnetic ordering found in MnO. With the use of the divalent Mn form factor[15] the magnetic intensities are reasonably well satisfied by a moment of $(4.45\pm0.15)\mu_B$ per metal atom, directed perpendicular to the unique [111] axis. The agreement between calculated and observed values is presented in Table I. It should be pointed out that, just as observed by Roth[10] in MnO, there is a diffuse base around the (111) reflection (particularly noticeable in Fig. 3). In both this composition and the following, it has been assumed that this diffuse scattering is traceable to domain effects in the structure, and the diffuse intensity is included with the coherent. The Néel temperature of the antiferromagnetic state is found to be about 83°K by measuring the intensity of the principal

[13] R. R. Heikes and W. D. Johnston, Bull. Am. Phys. Soc. **3**, 98 (1958).
[14] S. J. Pickart and R. Nathans, Phys. Rev. **116**, 317 (1959).
[15] L. Corliss, N. Elliott, and J. Hastings, Phys. Rev. **104**, 924 (1956).

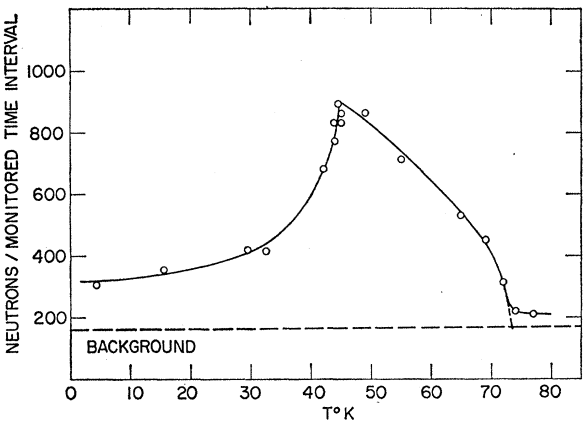

FIG. 5. Temperature dependence of the (111) intensity in $Li_{0.07}Mn_{0.93}Se$.

superlattice reflection as a function of temperature (see Fig. 2).

Because the material exhibits a weak magnetization[6] of $\sim0.2\,\mu_B$ below 100°K, the scattering was examined as a function of an external field in an attempt to determine whether the moment is of ferrimagnetic or ferromagnetic origin. The structure factors for the MnO-type ordering are such that any ferromagnetic moment will scatter into reflections with h, k, l even, while a ferrimagnetic moment must appear also (in sum) in reflections with h, k, l odd. If the moment can be turned along the scattering vector, however, the magnetic scattering amplitude becomes zero. As may be seen in Fig. 3, there was no effect on the Bragg reflections within the uncertainty of the measurements in a field of 5200 oe at 64°K. The implications of this result will be discussed in a later section.

$Li_{0.07}Mn_{0.93}Se$

Even though the increase in lithium content over the preceding composition is small, a different behavior was observed. Reference to Fig. 4 shows that the type

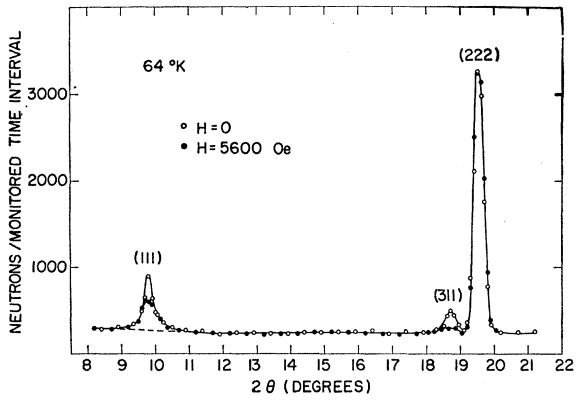

FIG. 6. Low-angle portion of the diffraction pattern of $Li_{0.07}Mn_{0.93}Se$ with and without a magnetic field applied along the scattering vector.

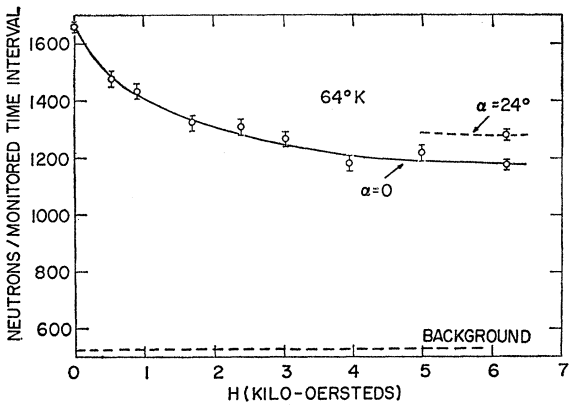

FIG. 7. Peak height of the (111) reflections in $Li_{0.07}Mn_{0.93}Se$ as a function of external field. α=the angle between the scattering vector and the applied field.

of magnetic ordering is the same, but that the relative intensity of the (111) and ($\bar{3}11$) superlattice reflections changes between 65° and 4.2°K. One possible explanation for this is a change of spin axis. If one assumes a unique spin axis, the ratio of these two intensities is fairly sensitive to the angle between it and the [111] direction. At 65°K the (111) and ($\bar{3}11$) intensities are in the proper ratio for the spins lying within (111) planes, while analysis of the data taken at 4.2°K (Table II) shows that a satisfactory model is one with the spins lying about 32° off the rhombohedral axis. Powder measurements determine only the inclination of the spins relative to the unique crystallographic axis, but it may be pointed out that [110], at 35.3° from [111], would come quite close to satsifying the intensities observed at 4.2°K. A measurement of the temperature dependence of the (111) reflection (Fig. 5) locates the spin axis change at about 45°K and the Néel point at 73°K. The magnitude of the moment at 4.2°K is $(4.25\pm0.10)\mu_B$ per metal atom, when calculated with the Mn^{2+} form factor.

The consequences of introducing multiple spin axes into fcc lattices having the second kind of ordering have been explored by Roth.[10] Because of the superposition of powder intensities, it may happen that several structures are equally compatible with the observations. In the present case, the data below 45°K are in satisfactory agreement with the model discussed by Roth in which three of the antiferromagnetic substructures making

TABLE I. Calculated and observed magnetic intensities for $Li_{0.05}Mn_{0.95}Se$ at 4.2°K. The moment is 4.45 μ_B and the spins are in (111) planes.

hkl	Observed	Calculated
(111)	801	827
($\bar{3}11$)	247	229
(33$\bar{1}$)	128	137
(511,333)	104	108
(5$\bar{3}$1)	56	54

TABLE II. Calculated and observed magnetic intensities for $Li_{0.07}Mn_{0.93}Se$ at 4.2°K. The calculations are made assuming μ=4.25 and an angle between the spin axis and the [111] direction of 32°.

hkl	Observed	Calculated
(111)	198	197
($\bar{3}11$)	330	319
(33$\bar{1}$)	95	95
(511,333)	41	48
(5$\bar{3}$1)	71	69

up the lattice have their spins in (111) planes with directions [$\bar{1}$10], [0$\bar{1}$1], and [10$\bar{1}$], while the fourth is directed along [111]. Since single crystal measurements are required to determine the structure uniquely, the interesting possibility of a transition between a single- and multiple-axis structure cannot at present be excluded.

This composition was also measured at 64°K with a magnetic field to investigate the origin of the measured moment[6] of about 0.5 μ_B. As shown in Fig. 6, the superlattice reflections were noticeably decreased in this case by the field. The (111) peak height is plotted as a function of field in Fig. 7. The effect is clearly saturated, but when the magnet is rotated in the azimuthal plane 24° away from the scattering vector, the decrease observed upon applying the field is smaller. Although this behavior would be expected of a (partially) ferrimag-

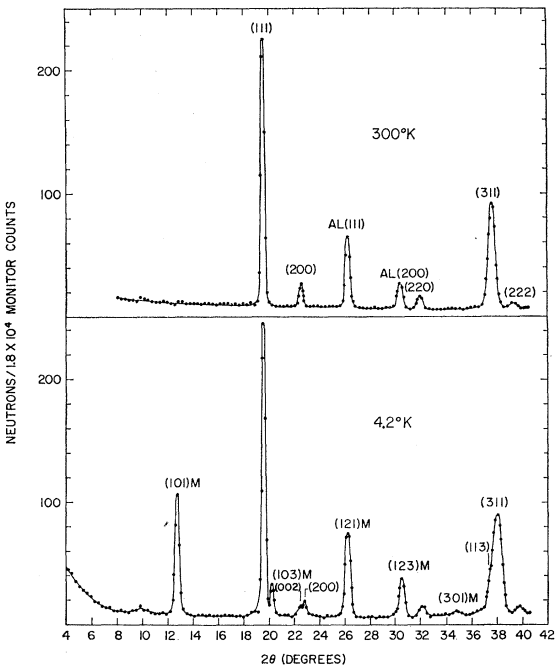

FIG. 8. Diffraction patterns of $Li_{0.10}Mn_{0.90}Se$ at 300°K and 4.2°K. Superlattice peaks (labeled *M*) in the latter case are superposed on reflections from the aluminum sample holder. The weak superlattice reflection observed near 10° in the low-temperature pattern might easily be due to a small contamination of antiferromagnetic MnSe.

TABLE III. Effect of an applied field on the coherent reflections in $Li_{0.10}Mn_{0.90}Se$ at 77°K.

hkl	Peak counting rate $H=0$	$H=4700$ oe	Background[a]
(111)	22 152±150	21 478±145	2395±49
(200)	10 938±104	10 337±101	5708±75

[a] No change in background measured with and without field.

netic material, other mechanisms (as will be discussed later) may be compatible with the data.

$Li_{0.10}Mn_{0.90}Se$

The diffraction data obtained for this compound at 300° and 4.2°K are shown in Fig. 8. Very little difference was observed between the room temperature pattern and one scanned at liquid nitrogen, although the sample possesses a spontaneous moment of 0.71 μ_B per molecule at the latter temperature.[6] This result implies that the moment is of ferromagnetic origin since the relative amount of magnetic scattering in that case would be small. To provide further confirmation of this point, the peak counting rates of the coherent reflections were measured with and without a magnetic field. The accumulated counts for the (111) and (200) reflections are listed in Table III. Scaled on the nuclear scattering from the same peaks, the observed decreases are appropriate to a ferromagnetic moment of (1.4±0.5) μ_B per metal atom, which, considering the difficulty of obtaining experimental precision, is felt to be in satisfactory agreement with the magnetization results.

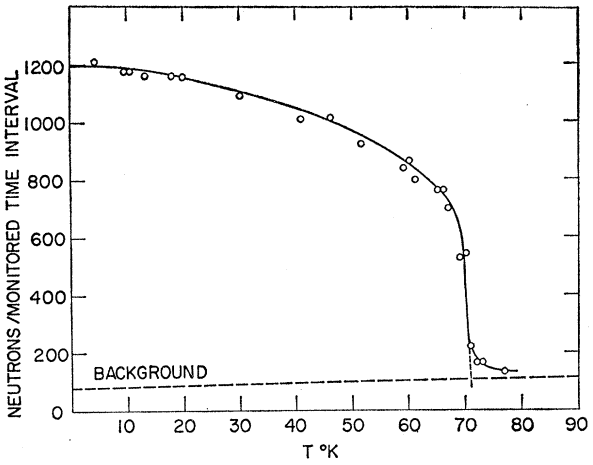

FIG. 10. Temperature dependence of the (101) superlattice intensity in $Li_{0.10}Mn_{0.90}Se$. Data were taken while sample was being both cooled and warmed.

The low-temperature data in Fig. 8 indicate a spin structure different from the preceding compositions; they are in fact indicative of the third type of fcc antiferromagnetic ordering, first observed by Corliss, Elliott, and Hastings[15] in the cubic zincblende phase of MnS. In this scheme the spins alternate in sign along only one cube edge, resulting in a tetragonal cell with $c=2a$, on which the magnetic reflections in the figure are indexed. The structure factors permit only reflections with $h+k$ odd and l odd to be observed. For a single axis model, the best agreement between observed and calculated intensities is obtained for an angle between the spin direction and the tetragonal axis of 45°, especially if one considers the sensitive ratio $I(101)/I(103)$. The moment per metal atom for this model is found to be (4.15±0.10)μ_B. Comparison of the observed intensities with those calculated for this and other spin directions is given in Table IV.

The possibility of multiple axis structures must also be considered in this case of the third kind of ordering.

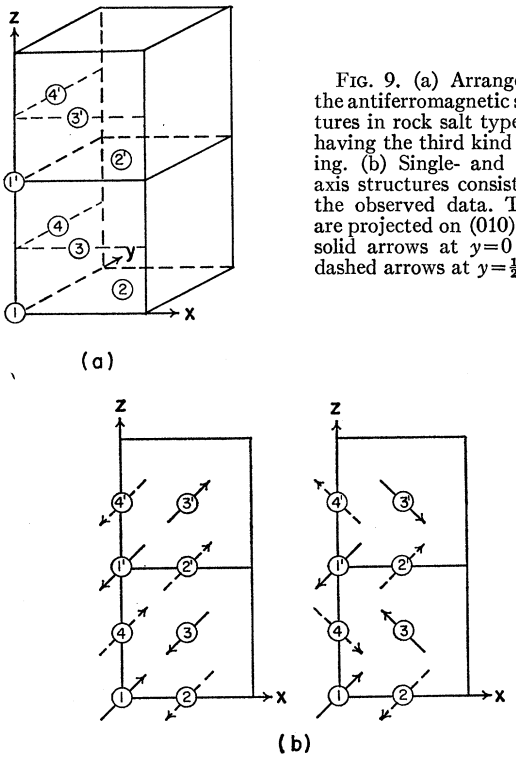

FIG. 9. (a) Arrangement of the antiferromagnetic substructures in rock salt type crystals having the third kind of ordering. (b) Single- and multiple-axis structures consistent with the observed data. The spins are projected on (010) with the solid arrows at $y=0$ and the dashed arrows at $y=\frac{1}{2}$.

Table IV. Observed and calculated magnetic intensities for $Li_{0.10}Mn_{0.90}Se$ at 4.2°K. The moment is 4.15 μ_B; various choices for the spin direction are shown. (ϕ is the angle between the spin direction and the tetragonal c axis.)

hkl	Observed	Calculated Spin direction: $\phi=0$ [001]	26.5° in (101)	45° [102]	90° in (001)
(101)	411	479	454	418	359
(103)	97	52	70	98	143
(121)	102[a]	127	115	99	70
(123)	55[a]	50	49	48	47
(301)	14	16	14	14	8

[a] After subtracting contribution from Al (111) and (200) reflections.

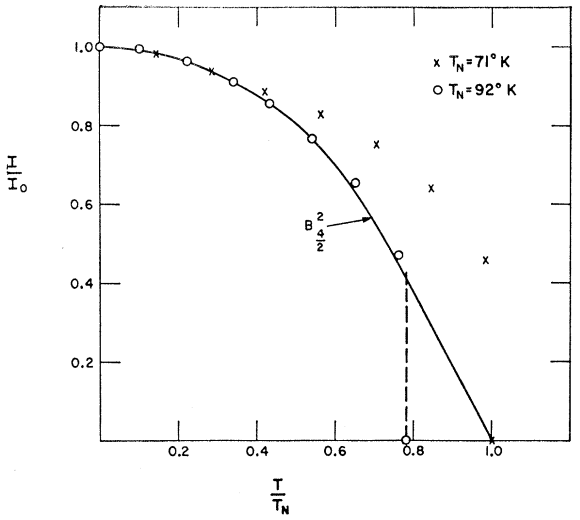

FIG. 11. Comparison of the experimental intensity vs temperature curve in Fig. 9 with the square of the Brillouin function for spin 4/2.

The generalized magnetic structure factor may be written

$$\mathbf{F}_m(hkl)=\sum_{j=1}^{8} p_j\mathbf{q}_j e^{2\pi i(hx_j+ky_j+lz_j)},$$

where the sum is over the eight magnetic ions obtained by doubling the lattice parameter along one of the cubic axes. (Here $p_j=0.539S_jf\times10^{-12}$ cm and $\mathbf{q}_j=\boldsymbol{\varepsilon}\times\boldsymbol{\varepsilon}\times\mathbf{S}_j$, where $\mathbf{S}_j$ is the spin vector of the ion and $\boldsymbol{\varepsilon}$ the normal to a given plane *hkl*.) Under the assumption that the $|S_j|$ are equal, the absence of reflections with l odd leads to the result

$$\mathbf{F}_m(hkl)/2p=\mathbf{q}_1+\mathbf{q}_2e^{\pi i(h+k)}+\mathbf{q}_3e^{\pi i(h+\frac{1}{2}l)}+\mathbf{q}_4e^{\pi i(k+\frac{1}{2}l)},$$

the lattice being decomposed into four tetragonal antiferromagnetic sublattices, as shown in Fig. 9(a). In like manner, extinction of reflections with $h+k$ even reduces the possible number of arbitrary axes to two. One finds that

$$F_m(hkl)/4p=\mathbf{q}_1+(-1)^hi^l\mathbf{q}_3,$$

showing that the two remaining spin directions are not correlated. A calculation of $\langle q^2\rangle_{\{101\}}$ and $\langle q^2\rangle_{\{103\}}$ for $\mathbf{S}_1$ along [102] and $\mathbf{S}_3$ along [$\bar{1}$02] then gives, as expected, identical results with the uniaxial model having its spin direction along [102]. The observed magnetic intensities are therefore equally consistent with either the uni- or multiple-axis model illustrated in Fig. 9(b). Furthermore, $\mathbf{S}_3$ could equally well be placed || to [012], so that the sublattice moments are not necessarily coplanar.

To investigate further the indicated ferromagnetic-antiferromagnetic transition, the temperature dependence of the intensity at the (101) position was measured. According to the results plotted in Fig. 10 the antiferromagnetic order disappears rather suddenly near 71°K, which agrees closely with the temperature at which the spontaneous moment arises. These intensity data can be matched with the square of a Brillouin function for spin 4/2 only if an appreciably higher Néel temperature is assumed (see Fig. 11), in confirmation of the fact that the transition is not the usual one from the antiferromagnetic to the paramagnetic state.

Another feature of low-temperature data to be noted is the splitting of some of the nuclear reflections, for example (200) and (311), which suggests a crystallographic distortion. This distortion was observed in a pattern taken at 65°K and probably occurs at the transition temperature. The deformation appears to be tetragonal with $c/a\sim1.02$, but this result is somewhat questionable because of the lack of resolution. Since the magnetic reflections are not split, the spacing of (*hkl*) and (*khl*) planes are equal, and the unique crystallographic and magnetic axes are the same; that is, the distortion is along the direction in which the spins alternate in sign.

The dependence of the transition temperature on an external field is presented in Fig. 12. Although the field does not affect the antiferromagnetic reflections when applied after the ordering has occurred, the transition temperature is lowered when the material is cooled in the field. As one might expect, the decrease is linear with H since the free energy of the cubic ferromagnetic phase is lowered by an amount μH.

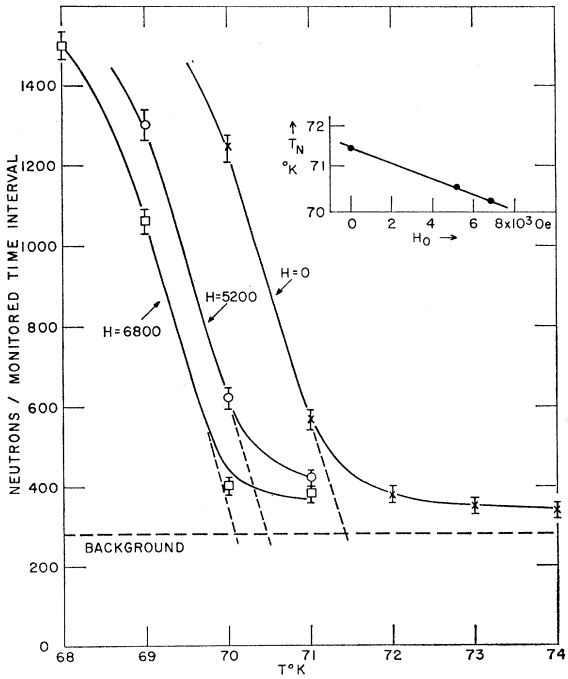

FIG. 12. Effect of an external field on the intensity vs temperature relationship of the (101) superlattice reflection in $Li_{0.10}Mn_{0.90}Se$. The insert shows the linear dependence of the transition temperature on the applied field. Data were taken on cooling only.

III. DISCUSSION AND CONCLUSIONS

It is apparent from the foregoing description that the magnetic ordering phenomena in the mixed crystal system $Li_xMn_{1-x}Se$ are quite sensitive to the lithium concentration, even though dilute. Some aspects of the neutron diffraction measurements that are relevant to the magnetic phase diagram of this system require further comment.

For the sample with five percent lithium, it should be noted that the intensity contributed to the nuclear reflections by a ferromagnetic moment as small as $0.2\ \mu_B$ could hardly be detected. However, the lack of a field effect on the superlattice reflections would seem to eliminate a ferrimagnetic alignment, unless the anisotropy is large. No other clue to the origin of the weak moment observed by magnetic measurements is provided by the neutron data.

In the ten percent composition, the ferromagnetic-antiferromagnetic transition is substantiated by both types of experiment. The decrease of the Bragg reflections by the field in the ferromagnetic phase is not consistent with a field-induced magnetization; any induced moment (since aligned along the scattering vector) would not scatter coherently, and no change would be observed upon applying the field. The influence of the double exchange interactions even below the temperature where the ferromagnetism is destroyed may be responsible for the fact that the ordering adopted has a next nearest neighborhood that is two-thirds ferromagnetic, rather than completely antiferromagnetic as in ordering of the second kind.

In the compound with $x=0.07$, the decrease of the supposedly antiferromagnetic reflections by an external field denotes a more complicated behavior. As noted above, such behavior would be observed in an antiferromagnetic material if some of its domains possessed an uncompensated moment which could be used to align the spins; a ferrimagnetism of this type, however, must have its origin in ordering of the Li^+ or Mn^{3+}, which is not borne out by quenching experiments on this sample.[6] (No information about ordering can be obtained from the magnetic or nuclear intensities because the effects are too small to be observable.) A field-induced anisotropy transition may also be ruled out, since the directional term q^2 in the magnetic structure factor decreases for the (111) reflection and increases for $(\bar{3}11)$ as the spins are tilted out of the (111) planes. However, it would be difficult experimentally to distinguish between a ferrimagnetic model or one in which the superlattice intensity is diminished by actually uncoupling some of the spins from the antiferromagnetic matrix. A possible mechanism for this process will be suggested in what follows.

De Gennes[16] has recently investigated the effect of double exchange on the spin configuration of layer and chain type antiferromagnetic structures. He finds that,

[16] P.-G. de Gennes, Phys. Rev. **118**, 141 (1960).

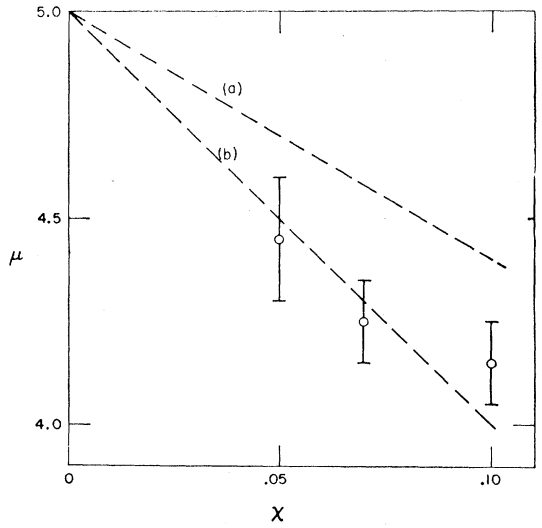

FIG. 13. The moment per metal ion as a function of x in $Li_xMn_{1-x}Se$. Dashed line (a) would result if the Mn^{3+} moment is $4\ \mu_B$, line (b) if $0\ \mu_B$.

because of the dependence of the hole transfer energy on the angle between neighboring ionic spins, the ground-state energy is lowered if the angle between sublattices (antiparallel in the unperturbed state) becomes less than π. It is necessary to distinguish between this situation, referred to as a "canted"-spin arrangement, and a multiple-axis structure such as discussed above, in which the several substructures remain antiferromagnetic within themselves but adopt more than one spin direction relative to the crystal axes. The canted lattice gives rise to ferromagnetic lattice reflections in addition to the antiferromagnetic superlattice reflections; the latter gives rise to no new reflections, but the relative intensities may differ from the single axis structure. As the temperature is raised, the canted arrangement is expected to revert to either a ferromagnetic or antiferromagnetic lattice at some intermediate transition temperature, depending on the exchange interactions and the impurity concentration.

The double-exchange mechanism as treated by de Gennes could therefore account both for the spontaneous moment observed in these compositions and for the ferromagnetic-antiferromagnetic transition. Since no ferromagnetic contribution was observed in the fundamental reflections, the canted-spin arrangements are consistent with the neutron data only for a slight departure from antiparallelism if the lattice is uniformly canted; alternatively, the distortions may be localized at dilute impurity sites. In either case there is little change in the coherent neutron intensities compared with a long-range antiferromagnetically ordered lattice. The second alternative is probably to be favored on physical grounds because of the low impurity concentration, and, as de Gennes points out, could be more profitably analyzed by studying the diffuse scattering

around the superlattice peaks. In the immediate neighborhood of such a local spin distortion, the superexchange coupling is considerably weakened by the presence of the double exchange, so that the cluster as a whole, which has a ferromagnetic component, can be acted upon by an external field. The decrease of the antiferromagnetic reflections in the $x=0.07$ compound and the apparent saturation with increasing field can simultaneously be accounted for by this means. Furthermore, the anisotropy transition at 45°K may perhaps be connected with a spontaneous ordering of the clusters, which is expected to occur because of the coupling between the local unbalanced moments.

Aside from the production of double exchanges, the trivalent manganese in the lattice also bears discussion because of its influence on the magnetic moment. The high-temperature susceptibility[6] of these compounds indicates that Mn^{3+} contributes nothing to the effective paramagnetic moment, and one may ask whether this is true in the ordered state as well. The average moments obtained from the diffraction data, plotted as a function of composition in Fig. 13, indicate that the Mn^{3+} moment must be fairly small. The origin of this diamagnetism could be either an unquenched orbital contribution which cancels the spin moment, or a spin moment which is itself quenched because of crystalline field effects.

Although the crystalline distortion observed for the ten percent sample is related to the configurational symmetry of the magnetic lattice, it is noticeably larger than the rhombohedral distortions expected in the other compositions, which are not observable with the present resolution. A tetragonal distortion (if more precise x-ray measurements confirm this symmetry) does not fit in with the hypotheses of either exchange[17] or anisotropy[18] magnetostriction, which have been proposed to explain the structure deformations in antiferromagnets. Another possible origin of the distortion, unrelated to the magnetic structure, is the cooperative ordering of individual oxygen octahedra coordinating the Jahn-Teller Mn^{3+} ion. This distortion has the correct direction ($c/a>1$), but one would not expect to find the critical fraction of Mn^{3+} necessary to produce macroscopic effects as low as one-tenth in the light of observations on other structures.[19]

IV. SUMMARY

The introduction of lithium into the rock salt lattice of MnSe exerts a substantial influence on the magnetic structure. The substitution initially lowers the transition temperature of the second kind of fcc ordering; at seven percent lithium an anisotropy transition is observed and the magnetic scattering is field dependent; finally, when the lithium concentration reaches ten percent, the composition becomes ferromagnetic as the temperature is lowered and subsequently undergoes a transition to antiferromagnetic ordering of the third kind. In the absence of single-crystal data, the presence of multiple antiferromagnetic axes in this system must be considered a possibility. Certain features of the data are in accord with a model of canted-spin lattices resulting from double exchange, if the angle of canting is small or the distortions are localized at dilute impurity sites.

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[17] J. S. Smart and S. Greenwald, Phys. Rev. **82**, 113 (1951).
[18] Y. Y. Li, Phys. Rev. **100**, 627 (1955).
[19] D. G. Wickham and W. J. Croft, J. Phys. Chem. Solids **7**, 351 (1958).