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Exchange Anisotropy in Mixed Manganites with the Hausmannite Structure

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Magnetic properties are reported of powder compounds isomorphous to hausmannite, but containing partial to nearly complete substitution of diamagnetic Zn^{2+} or Mg^{2+} ions in the tetrahedral sites of Mn_3O_4. X-ray diffraction of these compounds reveals a single phase, whose structure corresponds to a tetragonally distorted spinel. Unidirectional anisotropy is present and is detected by the observation of hysteresis loops displaced along the field axis when the materials are cooled to low temperatures in magnetic fields of several kilo-oersteds. The unidirectional behavior is stable to reverse field pulses of 140 koe. An exchange anisotropy model is proposed involving interactions between ferrimagnetic and nearly antiferromagnetic regions brought about by the random distribution of the diamagnetic ions among the tetrahedral sites and the consequent magnetic inhomogeneity. This model is similar to that proposed for disordered alloy systems. Magnetic viscosity effects are observed which correspond in part to ordinary magnetic viscosity, but which are influenced by the presence of unidirectional anisotropy. The identity of this anisotropy is not impaired by the ordinary viscosity effects. In addition, observations of certain differences in the hysteresis loops measured dynamically and quasi-statically reveal an "extraordinary" viscosity associated with a gradual breakdown of the unidirectional anisotropy.

INTRODUCTION

THE properties of manganite compounds having a crystal structure isomorphous with the mineral hausmannite, Mn_3O_4, have lately attracted attention. The magnetic properties form one center of interest and are the concern of the present work. Recent studies have been concerned with both the paramagnetic[1,2] and the ferrimagnetic behavior.[3–5] Another source of interest centers on their crystallographic properties and the origin of the tetragonal distortion from the cubic spinel structure.[6–8]

In this paper we shall report and discuss certain features of the magnetic behavior of compounds with the formula $(D_x\mathrm{Mn}_{1-x})\mathrm{Mn}_2\mathrm{O}_4$ formed by partial substitution of the diamagnetic ions Zn^{2+} and Mg^{2+} for the Mn^{2+} ions in Mn_3O_4. Studies of magnetization[4,5] and magnetic structure[9,10] have confirmed that these compounds possess a ferrimagnetic arrangement of the general type suggested by Yafet and Kittel[11,12] with canted spins on the octahedral sites for $x<1$. The details of these structures are still the subject of investigation.[5,13] The compounds at the end point $x=1$, $ZnMn_2O_4$ and $MgMn_2O_4$, appear to be antiferromagnetic on the bases of susceptibility[1] and neutron diffraction[10] studies. However, their Néel temperatures are not clearly defined although they seem to be in the range of 100°–200°K.

In part these manganite systems are similar to the nickel-zinc ferrite system considered by Grimes *et al.*[14] These authors noted that the molecular field fluctuations arising from microscopic composition variation would produce a system consisting of ferrimagnetic regions immersed in a paramagnetic mesh. In the present investigation of manganites, it is proposed that at the temperatures of interest there is a coexistence of regions of ferrimagnetic and antiferromagnetic order.

We report herein the observation of magnetic hysteresis loops displaced from their symmetrical positions about the origin, which occur upon the cooling in a magnetic field to low temperatures, of mixed manganites $(D_x\mathrm{Mn}_{1-x})\mathrm{Mn}_2\mathrm{O}_4$, where D is Zn or Mg and $0<x<1$. The loop displacement is almost wholly along the field axis. These observations are attributed to exchange anisotropy interactions between ferrimagnetic and antiferromagnetic regions, as discovered in Co-CoO by Meiklejohn and Bean[15] and extended to other systems including alloys.[16] We have also observed magnetic viscosity effects on these compounds similar, in part, to the report for Mn_3O_4 by Menyuk and Dwight,[5] but related, in part, to the displaced loop phenomena. Experiments and discussion are directed toward the elucidation of ordinary magnetic viscosity, unidirectional anisotropy, and an "extraordinary" viscosity associated with this anisotropy. It is concluded that the presence of the various phenomena does not negate their separate identities in these materials. A note of caution is sounded regarding the interpretation of some pulsed-field hysteresis data.

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[14] D. M. Grimes, S. Legvold, and E. F. Westrum, Phys. Rev. **106**, 866 (1957).

[15] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 1413 (1956); and **105**, 904 (1957).

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DISPLACED LOOP BEHAVIOR

The compounds studied are powders prepared by standard ceramic techniques as described earlier.[4] For Zn substitution, the values of x are approximately 0.3, 0.5, and 0.75. (Analyzed compositions appear in reference 3, except for the last which is $Zn_{0.76}Mn_{2.24}O_{3.65}$). For Mg substitution, the value of x is 0.5. In all cases, x-ray diffraction patterns indicate a single phase. All of these compositions have approximately the same tetragonal distortion from the spinel structure ($c/a=1.15\pm0.01$). Previous work has established that they are "normal" in the usage for spinels, in that there are only Mn^{3+} ions on the octahedrally coordinated B sites. The tetrahedral A site occupation is thus ($D_x^{2+}Mn_{1-x}^{2+}$).

Magnetization curves and hysteresis loops to 10 koe were taken between liquid helium temperatures and room temperature in the apparatus described previously.[17] The magnetization vs temperature curves at fixed fields are shown in Fig. 1. The existence of fairly definite Curie temperatures for each of the compositions is evidence that single magnetic phases have formed, in contrast to gross mixtures of the end-point compositions. Alternately, one may note an increasing diffuseness of the Curie point for increasing x, i.e., fraction of nonmagnetic ion substitution in the A sites. This is in accord with the suggestion and data of Grimes *et al.*[14] that the concept of a *single* Curie temperature becomes meaningless as the spatial fluctuations in magnetic occupation of the A sites increase. A related approach to this problem is contained in the examination of the number of magnetic linkages and the distribution thereof, as carried out recently by Gilleo[18] and indicated in early work of Néel.[19]

Also shown in the figure is the behavior of the reciprocal of the initial volume susceptibility near to and just above the Curie point. While the temperature intercept of each χ_0^{-1} vs T curve may be taken as an average Curie point, it is of interest to observe that the remanent magnetization often does not vanish until slightly higher temperatures are reached. This effect increases with larger values of x and presumably is another manifestation of the spatial fluctuations in magnetic occupancy of the A sites.

These magnetization measurements were made after cooling the samples to liquid helium temperature in the absence of any applied magnetic field, other than the "earth's field" in the laboratory. (This condition will be designated "cooled in zero field.") Many of the M vs T curves show a maximum value at low

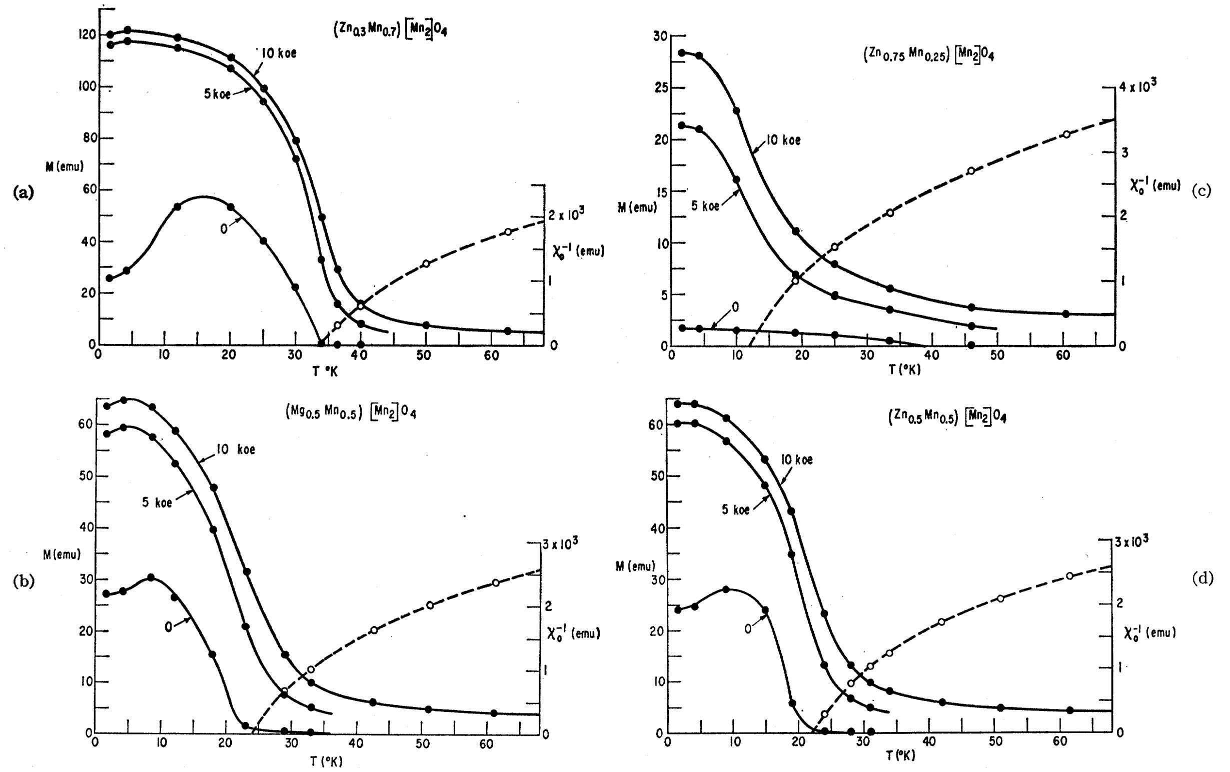

FIG. 1. Magnetization at various fields (solid curves) and the inverse initial susceptibility (dashed curves) as functions of temperature for different manganite compounds.

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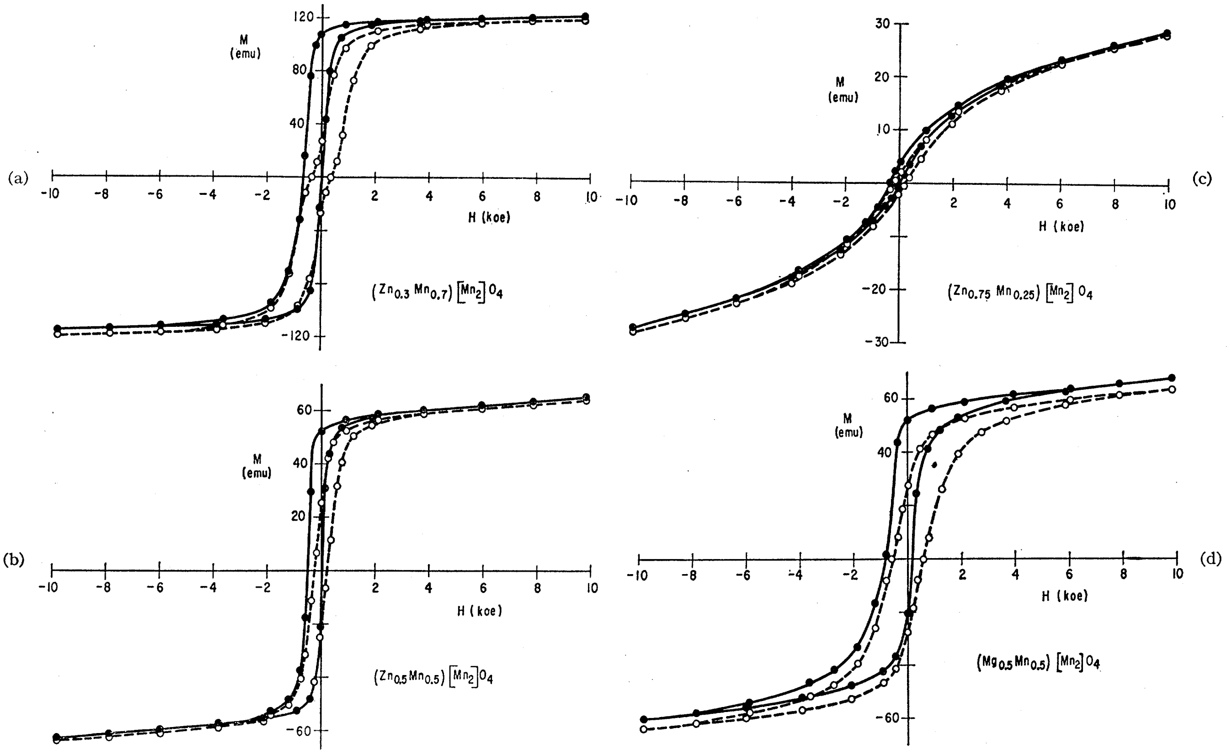

FIG. 2. Hysteresis loops measured at 1.8°K for different manganite compounds cooled in +5 koe (solid curves) and in zero field (dashed curves).

temperature, in contrast to the monotonic behavior normally (but not always) expected. This is particularly prominent in the remanent magnetization data, taken during field cycles between plus and minus 10 koe. This behavior is reminiscent of the behavior shown by disordered alloys of about 25% Mn in Ni, Co, Cu, and Ag,[16] or of any system with an anisotropy which increases markedly with decreasing temperature. If these samples are cooled to low temperature in an applied field of a few kilo-oersteds, the expected monotonic behavior of these curves is produced.

For most of these samples the magnetization curves measured in very high pulsed fields were reported in a previous paper.[4] A similar experiment on the $x=0.75$ Zn-substituted sample yields a spontaneous moment of $m_0=(0.26\pm0.03)$ μ_B/molecule and a differential volume susceptibility equal to $(3.2\pm0.4)\times10^{-4}$ emu between 40 koe and 140 koe. In view of the observation of very high anisotropy fields in Mn_3O_4 by Dwight and Menyuk,[5] these powder values probably need to be interpreted as indicated earlier.[4,5]

The hysteresis loops obtained at 1.8°K, when the samples were cooled in a field of 5 koe and measured parallel thereto, are presented in Fig. 2, along with the comparable loops for zero field of cooling. The loops obtained after field cooling are displaced from their usual symmetrical positions about the origin but, within a few percent, give equal and opposite magnetizations for $H=\pm10$ koe. The behavior of these compounds is a clear example of an exchange anisotropy mechanism[15,16] operating in these mixed manganite systems. We shall defer discussion of possible origins to a later section.

The temperature dependence of the displaced loops may aid in understanding the behavior. The displacement can be characterized by the asymmetry in coercivity and/or that in the remanence.[15,20] The curves in Fig. 3 represent the negative of the algebraic average of the two coercivities, $-\bar{H}_c$, as a function of temperature. It is noteworthy that this measure of the displacement does not vanish until the Curie point is reached or, in some cases, exceeded, in contrast to the behavior in disordered alloy systems.

An attempt was made to "break" the displacement of the loop with high pulsed fields in both the Zn and Mg substituted compounds with $x=0.5$. The sample was cooled in +2 koe from room temperature to 4.2°K. The remanent magnetization (in zero applied field) was noted. The sample was subjected to a pulsed field of −140 koe, and the remanence measured again. A large asymmetry in these remanence values was found, as evidence of the field stability of the loop displacement. Observation of the magnetization during such a pulse revealed that the hysteresis curve was closed beyond several koe, and that the magnetization was

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[20] J. S. Kouvel and C. D. Graham, Jr., J. Phys. Chem. Solids 11, 220 (1959).

fully reversed (apart from the high-field susceptitility).

A corollary observation to the failure to "break" the displaced loops is that only a small isothermal remanence can be established by large pulsed fields on a sample originally cooled in zero field. Thus a 70-koe (0.05-sec) pulse produces, in the Zn-substituted sample, ($x=0.5$), a remanence about one-third of that acquired by cooling in a field of a few koe. By comparison, in Mn_3O_4, the isothermal pulsed-field remanence ($H_{\max}\gtrsim 20$ koe) is essentially the same as the thermoremanence acquired on cooling in a few koe to 4.2°K. This difference establishes the absence of a unidirectional anisotropy in Mn_3O_4.

MAGNETIC VISCOSITY BEHAVIOR

In connection with these experiments, magnetic viscosity effects were observed, and their presence raises the question as to how much the loop displacement is associated with the magnetic viscosity. Before presenting the results, we note that one may distinguish in principle between two kinds of magnetic viscosity in systems of the type under consideration. One of these is the ordinary viscosity studied by many investigators.[21–24] It manifests itself in a time lag between magnetization and magnetic field beyond that accountable for by eddy currents. The magnetization tends to change slowly in the direction of the most recent field change, and usually in the presence of a nonzero field. However, Néel[25] has emphasized that even in zero field the remanence of a magnetized sample will tend to decay toward the demagnetized condition which is the ultimate state of thermodynamic equilibrium. The other kind of magnetic viscosity is peculiar to systems exhibiting undirectional anisotropy. Thus we may again recognize that the ultimate state of thermodynamic equilibrium is that having not only a zero-area hysteresis loop, but also an undisplaced loop. On this basis a displaced hysteresis loop might move toward an undisplaced one for sufficiently long resting periods at appropriate fields. We shall designate this phenomenon as an extraordinary viscosity in what follows. In practice, the times necessary to reach the ultimate equilibrium states are frequently much greater than one cares to wait, and hence we have apparently stable hysteresis loops of nonzero area, both undisplaced and displaced.

It is interesting to speculate on an effect of combining these phenomena of ordinary magnetic viscosity, unidirectional anisotropy, and its characteristic extraordinary viscosity. If the latter viscosity has an extremely long-time decay behavior, it may be neglected in one approximation. The ordinary magnetic viscosity having, in general, a different origin, could still be important during times of interest. Thus, one might observe a displaced loop with the viscosity effects moving the state of the sample toward an ideal displaced loop as the apparent equilibrium, rather than toward the ultimate equilibrium state of an undisplaced loop.

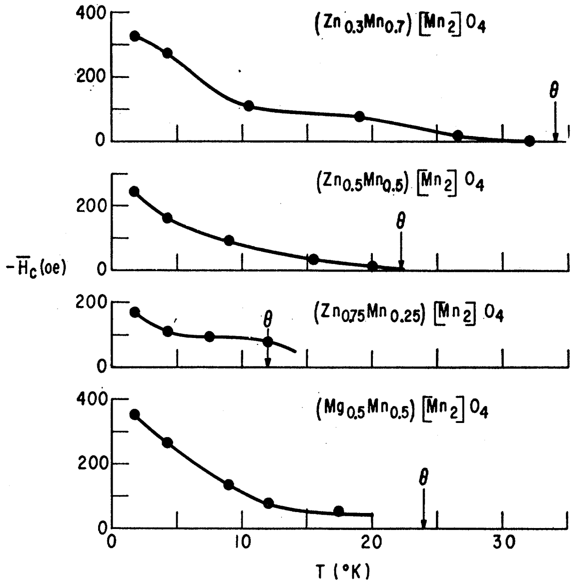

FIG. 3. The negative algebraic average of the coercive fields vs temperature for different manganite compounds cooled to 1.8°K in +5 koe. The Curie points, θ, derived from susceptibility data (Fig. 1), are indicated.

We consider now the viscosity effects observed, in the light of the preceeding remarks. Both Zn and Mg substitution gave similar behavior, with more data obtained for the former. The thermoremanent magnetization of the Zn-substituted $x=0.5$, sample, acquired on cooling in +2 koe from room temperature to 4.2°K, is observed to decay slowly with time, if the measurements are started immediately upon removal of the applied field, as shown in Fig. 4. During the decay, the internal field arising from the sample demagnetizing factor is about -30 oe. The form of the decay is $\Delta M=S\log t$, in accord with previous experiment and theory.[21–25] The decay continues at applied fields of -100 oe and -200 oe, with S increasing as dM/dH, taken from the hysteresis loop, increases. These decays fall naturally into the framework of the ordinary magnetic viscosity. They may also be attributed to some extent to an extraordinary viscosity involving a gradual disappearance of the loop displacement.

Following these measurements, the sample was subjected to a field pulse of +70 koe (~0.05 sec), restoring a large part but not all of the initial thermoremanence. This was followed by two such pulses to

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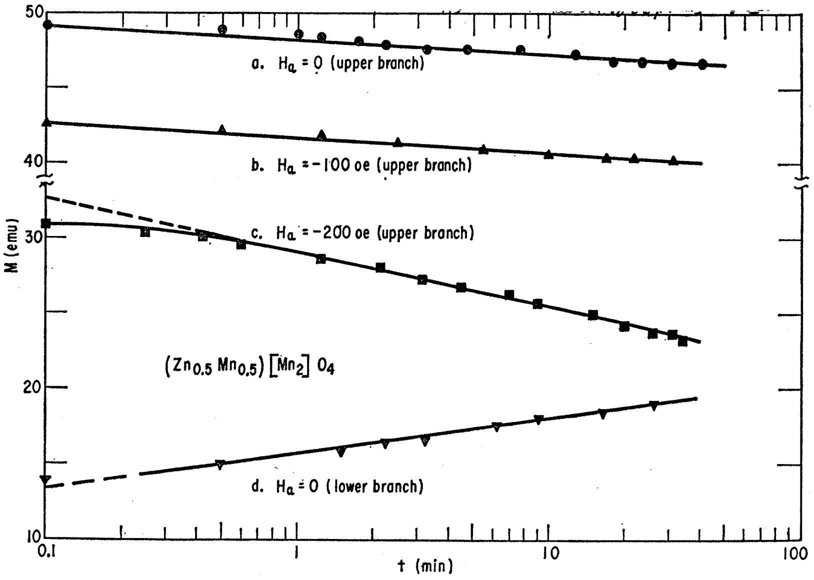

FIG. 4. Magnetization, measured at 4.2°K, as a logarithmic function of time. Measurement starts immediately after the applied field H_a is changed. Sequence as follows: a. After cooling from 300°K in +2 koe and removing field; b. H_a changed to −100 oe; c. H_a changed to −200 oe; d. H_a pulsed once to +70 koe, twice to −70 koe and then removed. These lower branch remanent magnetizations are positive in sign as indicated.

−70 koe after which the decay was again observed at the lower branch remanence point. This remanence is *positive* in sign and the decay consists of an *increase* in the magnitude of the magnetization, as shown in Fig. 4, notwithstanding the internal demagnetizing field of about −10 oe. While the sign of this decay is as expected from ordinary viscosity behavior for this branch of the hysteresis loop, the essentially field-free increase in the magnitude of the moment does not correspond to previous viscosity experience. Indeed, in order that it be inside the scope of ordinary viscosity phenomena, one must consider the addition of a relatively stable unidirectional anisotropy which raises the equilibrium remanence from zero to some positive value.

It may be noted that in this pulsed-field experiment, the value of the lower branch remanence is much closer to that of the upper branch than that found in the slowly measured loop shown in Fig. 2. Thus the loop displacement has been enhanced by the dynamic measurement. The difference in sign and value of the two lower branch remanences is in the opposite direction from that expected from ordinary viscosity. Hence we must attribute it to an extraordinary viscosity which is operative during the quasi-static measurements in negative fields and signifies a gradual breakdown of the unidirectional anisotropy.

There is yet another observation on these materials which follows from the discussion of viscosity effects. For pulsed field measurements there is an enhancement of the coercivity on the upper (descending) branch of the hysteresis loop (and of the loop displacement, if present) of a sample originally cooled to low temperature in a field, over that measured quasi-statically. This may be viewed as an extension of the demonstration by Street and Woolley[21] that the shape of the loop depends on the measurement method. It can be a consequence of either or both of the kinds of viscosity under consideration, but is observed in materials showing unidirectional anisotropy, as well as in those which do not. In the $x=0.5$ Zn-substituted sample the quasi-statically measured coercivity (upper branch) at 4.2°K after field cooling is 260 oe while the corresponding pulsed field value is 600 oe. The time rate of field change at the coercive point in the latter measurement was 5×10^6 oe/sec.

While Mn_3O_4 shows no unidirectional anisotropy, Dwight and Menyuk[5] have seen viscosity decay effects near the coercive fields at 4.2°K on a natural single crystal, and the present authors have seen similar decays on powders at 20°K in fields of −500 oe and −1000 oe. The pulsed field coercivity at 5.2°K for Mn_3O_4 powder was reported[4] to be 16 koe. From present considerations, the quasi-static value could be lower. Dwight and Menyuk comment on this, but it had not been appreciated at the time of earlier pulsed-field experiments.[26] The point is confirmed by our present observation that the quasi-static coercivity of the same Mn_3O_4 at 4.2°K is about 6 koe. The conclusion to be drawn from this digression is that coercivities measured by pulsed-field techniques should be interpreted with care.

In summary, the preceding description of results and of a phenomenological viewpoint shows that unidirectional anisotropy and magnetic viscosity are present more or less independently in these samples and that their coupling introduces additional effects without impairing the identity of either phenomenon. In other materials, it is possible to imagine that a

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[26] In Table I of I. S. Jacobs [J. Phys. Chem. Solids 11, 1 (1959)], all the large coercivities were measured with pulse techniques ($dH/dt \sim 5\times10^6$ oe/sec), while the small ones were determined quasi-statically on samples cooled in zero field.

stronger coupling between these phenomena could obscure their separate identities.

DISCUSSION

Menyuk *et al.*[27] have reported on a cobalt-vanadium spinel which shows both a compensation point and a hysteresis loop displaced with respect to the *magnetization* axis, upon field cooling to 4.2°K. The difference in the nature of the loop displacement between their sample and present materials suggests that somewhat different mechanisms are responsible. They note that a large nonunidirectional anisotropy might account, in part, for their findings. It is clear from the present experiments on the mixed manganites that the origin for the unidirectional behavior should be sought in the exchange anisotropy mechanisms proposed earlier for two-phase[15] and single-phase[16] systems.

Previous studies on these manganites have pointed to a significant antiferromagnetic interaction between the Mn^{3+} ions on the octahedral sites. Interactions between ions lacking in 180° superexchange linkages have been the subject of recent theoretical discussions[28–30] as well as a direct experimental measurement.[31] The tetrahedral sites of these compounds are randomly occupied by Mn^{2+} ions and diamagnetic Zn^{2+} or Mg^{2+} ions in the designated proportions. Such randomness is inherently marked by considerable spatial fluctuations in local composition, some small regions being rich in Mn^{2+}, others rich in the diamagnetic ions. Thus, when we examine the ferrimagnetically ordered state at very low temperature, it is reasonable to expect local magnetic structures varying from ones similar to that found for Mn_3O_4 to ones approaching those expected for DMn_2O_4. The latter local structures may resemble canted antiferromagnets.[32–34] Some of the gross behavior may be in accord with a single magnetic configuration intermediate between the end points,[4] but that approximation need not hold on a local scale. The existence of angles between the B-site moment directions and the net magnetization direction, makes possible a gradual variation in angle between differing local structures. Such regions are inherently exchange-coupled through the octahedral sites. If there is sufficient anisotropy associated with these sites, it is possible that an applied magnetic field can reverse the magnetization of those local structures contributing most of the net spontaneous magnetization, while leaving essentially unaffected the nearly antiferromagnetic configuration of those local structures having a negligible magnetization. If the latter structures are able to preserve their identity; i.e., the *sign* of their negligibly small contribution to the spontaneous moment, even in the presence of an applied field, they will serve to renucleate the original magnetic structure of the whole compound, when the applied field is removed. This description constitutes one way in which an exchange anisotropy mechanism can operate to produce unidirectional behavior in such mixed manganites. The model employed here has a number of similarities to that proposed for disordered alloys.[16]

What is lacking in this model is a means by which the nearly antiferromagnetic configurations acquire their preferred orientation and unique sign during the field cooling. It is tempting to suggest that all the arrangements are formed just at the ferrimagnetic Curie temperature, when the anisotropy forces are expected to be small. This suggestion would, however, be counter to the evidence of Fig. 3 that the loop displacement, and hence the anisotropy, persists right up to the Curie point. Consequently, the preferred orientation may be initiated at yet higher temperatures.

A conclusion of the Yafet-Kittel-Lotgering theory[11,12] is that a triangular ferrimagnetic configuration at 0°K cannot, in general, give way to a fully paramagnetic state as the temperature is increased, but must pass through either an antiparallel ferrimagnetic state, or one in which there is antiferromagnetism on one kind of site and paramagnetism on the other. While the theory of canted ferrimagnetic structures is still developing,[13] this qualitative feature appears intuitively correct and will probably remain. However, while there is as yet no clear demonstration of either of the above-noted transitions, it has been suggested[4,5] that Mn_3O_4 retains its triangular ferrimagnetic state to its Curie point and may go over to the mixed para-antiferromagnetic state. Moreover, when a field is applied to a manganite compound having this mixed state, it induces a ferrimagnetic or canted configuration which could include the postulated nucleating structures. These must not only form but must also stabilize in this temperature region above the Curie point. Preliminary experiments have been performed which indicate a stable nucleation occurring above the Curie point, and lend plausibility to the model proposed herein. Further work is in progress on this effect. An important question raised by the model concerns the nature and origin of the anisotropy required for stabilizing the responsible configuration.

There are several qualitative features of the composition dependence of the unidirectional behavior worth noting. These are in accord with the proposed model, or with any model based on local spatial fluctuations in composition. The occurrence of the loop

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[33] T. Moriya, Phys. Rev. **120**, 91 (1960).

displacement seems to require some minimum concentration of the diamagnetic ions on the tetrahedral sites. This probably reflects the necessity of having certain minimum-size clusters of diamagnetic ions, or regions rich in these ions. As the average diamagnetic ion concentration increases, however, there are decreases in (1) the ratio of the thermoremanent magnetization acquired on field cooling to the spontaneous magnetization[4] (or to the magnetization at 10 koe) and (2) the unidirectional anisotropy per Mn^{2+} concentration, estimated as the product of loop displacement $-\bar{H}_c$ times thermoremanent magnetization. These effects probably indicate the decrease in the size of regions rich in Mn^{2+} and the increasing fraction of more isolated tetrahedral Mn^{2+} ions, unable to acquire sufficient stability to participate in the exchange anisotropy phenomena.

The mixed manganite powders of present interest are far from ideal for a study of the origins of the observed viscosity effects. A better approach to the ordinary viscosity phenomena is the work of Dwight and Menyuk[5] on single crystals of Mn_3O_4. To supplement the framework of previous viscosity studies, Mn_3O_4 contributes a unique magnetic structure[9] (orthorhombic through doubling of one basal edge of the body-centered tetragonal cell) and an extremely high anisotropy energy for avoiding the tetragonal direction. To this system the mixed manganites can add spatially fluctuating molecular fields.

Considerably less is known about the extraordinary viscosity associated with unidirectional anisotropy. It presumably arises from magnetization processes in the antiferromagnetic phase or near-antiferromagnetic region of two-phase or single-phase systems. These could be coherent rotation, antiferromagnetic wall motion, Bloch line motion within walls, sublattice inversion, and perhaps others. The details of the particular magnetic structure would govern the dominant mechanism. It would be premature to apply any of these to the present system, in view of the lack of detailed understanding of the local magnetic structures.

CONCLUSIONS

We have reported herein certain magnetic properties of powder compounds isomorphous to hausmannite, but containing partial diamagnetic substitutions of Zn^{2+} or Mg^{2+} in the tetrahedral sites of Mn_3O_4. Exchange anisotropy is present and is detected by the observation of hysteresis loops displaced along the field axis when the materials are cooled to low temperature in magnetic fields of several koe. A model is proposed involving interactions between ferrimagnetic and nearly antiferromagnetic regions brought about by the random distribution of the diamagnetic substitutions. This model is similar to that proposed earlier for disordered alloy systems. Magnetic viscosity effects are observed which correlate in part to ordinary magnetic viscosity, but which also are associated with the unidirectional anisotropy. The connection does not impair the identity of the separate phenomena. In addition, observations of certain differences in the hysteresis loops measured dynamically and quasi-statically reveal an extraordinary viscosity associated with a gradual breakdown of the unidirectional anisotropy.

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