MATERIALS SCIENCE

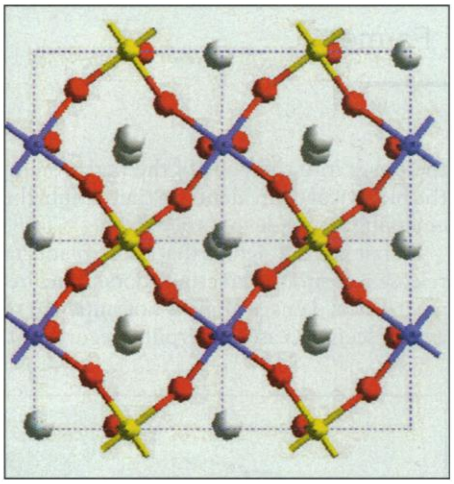
Charge Ordering in Manganates

C. N. R. Rao and A. K. Cheetham

Giant magnetoresistance (GMR)—the phenomenon whereby a magnetic field can dramatically alter the electrical resistance of a material—and related properties of the rare-earth manganates (*1*) have aroused great interest in recent months. Not only do these materials pose fascinating problems in physics, but they also possess properties of technological interest. Although a complete understanding of the GMR and other magnetically influenced transport properties of these materials will have to await further studies, we have come to learn of the importance of several kinds of electronic interactions and lattice coupling (*2*). Recent attention has turned to charge ordering of Mn^{3+} and Mn^{4+}, as distinct from spin ordering. This property and related phenomena exhibited by these manganates reveal some remarkable features with regard to charge and spin dynamics, in addition to opening up new avenues for research.

Charge ordering of Fe^{2+} and Fe^{3+} in Fe_3O_4 has been known for many years. It occurs at 120 K and below, where it coexists with the ferrimagnetic order that is established at a much higher temperature (T_c = 860 K). Charge ordering in $Ln_{1-x}A_xMnO_3$ (where Ln is a rare earth and A is a divalent cation), on the other hand, is more subtle because it competes with the double-exchange interaction, which favors ferromagnetism and metallicity (charge ordering inhibits the electron transfer process that is associated with double exchange and therefore cannot coexist with ferromagnetism in manganates). Manganese(III), being a Jahn-Teller ion, adds to the vivacity in behavior because the cooperative Jahn-Teller effect is associated with the charge-ordered state. The 1:1 Ln:A composition is of particular interest because charge ordering is more facile at this stoichiometric composition.

It has become clear that charge ordering in manganates exhibits a strong dependence on the average radius of the A-site cations, $\langle r_A \rangle$. A simple way to vary $\langle r_A \rangle$ smoothly is to change the rare-earth element in $Ln_{1-x}A_xMnO_3$, because $\langle r_A \rangle$ decreases down the rare-earth series, La to Lu (known as the lanthanide contraction). Changing the alkaline-earth element from Sr to Ca increases the range; thus, $La_{0.5}Sr_{0.5}MnO_3$ has an $\langle r_A \rangle$ of 1.26 Å and $Y_{0.5}Ca_{0.5}MnO_3$ has an $\langle r_A \rangle$ of only 1.13 Å. The general properties can be organized along a continuum of cation size, from largest to smallest. At the largest cation size ($\langle r_A \rangle$ > 1.24 Å) are the $Ln_{0.7}A_{0.3}MnO_3$-type manganates, which exhibit strong GMR and are dominated by double-exchange interactions and thus show no charge ordering. For slightly smaller cations, for example $Nd_{0.5}Sr_{0.5}MnO_3$ ($\langle r_A \rangle$ ~ 1.24 Å), a ferromagnetic metallic state (T_c ~ 250 K) similar to that seen in the strong GMR region transforms to an antiferromagnetic charge-ordered (and insulating) state at 150 K (T_N = T_{co}) (*3*). The small $\langle r_A \rangle$ regime is exemplified by $Y_{0.5}Ca_{0.5}MnO_3$ and $Nd_{0.5}Ca_{0.5}MnO_3$ (see figure), with $\langle r_A \rangle$ values of 1.13 and 1.17 Å, respectively; materials in this region do not exhibit ferromagnetism. The compound $Pr_{0.7}Ca_{0.3}MnO_3$ ($\langle r_A \rangle$ = 1.17 Å), for example, becomes charge-ordered at 200 K (T_{co}) and antiferromagnetic upon further cooling to 140 K (*4*). A more complex region of intermediate $\langle r_A \rangle$ is discussed below.



Structure of a charge-ordered manganate. This view down the *c* axis of $Nd_{0.5}Ca_{0.5}MnO_3$ at 10 K shows charge ordering of the Mn^{3+} and Mn^{4+} cations. Mn^{3+} is shown in blue, Mn^{4+} in yellow, oxygen in red, and Nd/Ca in whitish gray. [Figure courtesy of T. Vogt, Brookhaven National Laboratory]

The charge-ordered, insulating state in the manganates can be "melted" into the metallic (GMR) state by the application of magnetic fields, the temperature-field behavior depending on the size of the A-site cations (*5*). The size of the A-site cations presumably determines the Mn-O-Mn angles, thereby controlling the e_g bandwidth and the strength of the double-exchange mechanism. Accordingly, in $Y_{0.5}Ca_{0.5}MnO_3$, with its small A-site cations, not only does the charge ordering occur in the paramagnetic state at a relatively high temperature (T_{co} = 250 K; T_N ~ 140 K), but it is nearly impossible to destroy the robust charge-ordered state by the application of a magnetic field (*6*).

In the intermediate region of A-cation size, between about 1.17 and 1.22 Å, one observes complex charge ordering and magnetic properties. Fine tuning of the charge ordering by varying $\langle r_A \rangle$ is indeed possible, as revealed by the transitions from the charge-ordering to the ferromagnetic state found in $Nd_{0.5-x}Sm_xSr_{0.5}MnO_3$ (*5*) and $Nd_{0.25}La_{0.25}Ca_{0.5}MnO_3$ (*6*). In $La_{0.5}Ca_{0.5}MnO_3$ ($\langle r_A \rangle$ ~ 1.20 Å), a ferromagnetic to antiferromagnetic transition occurs (T_c ~ 225 K; T_N ~ 170 K), accompanied by a commensurate to incommensurate charge-ordering transition, illustrating once more the delicate interplay between charge and spin (*7*). Magnetic domain boundaries seem to break the coherence of the spin ordering on the Mn^{4+} sublattices as well as the identity of the two sublattices; it appears that commensurate long-range charge ordering coexists with quasi-commensurate orbital ordering.

The delicate balance between charge ordering, antiferromagnetism, and ferromagnetism, and its dependence on $\langle r_A \rangle$, can be understood qualitatively in terms of the variations of the various interaction terms with the Mn-O-Mn angle. The ferromagnetic and antiferromagnetic exchange coupling constants J_{FM} and J_{AFM} decrease with diminishing $\langle r_A \rangle$, the former more rapidly than the latter (*8*). On the other hand, the single-ion Jahn-Teller energy E_{JT} must be invariant with A-cation size. The largest $\langle r_A \rangle$ region, therefore, is dominated by the large J_{FM} and only ferromagnetism is observed. In the regime of slightly smaller cation size, however, J_{AFM} > J_{FM} and ferromagnetism gives way to antiferromagnetism on cooling. The e_g electrons, which are localized magnetically, further lower the configuration energy by undergoing charge ordering that coexists with the antiferromagnetic state. Such a state should be sensitive to magnetic fields. In the small $\langle r_A \rangle$ regime, the cooperative Jahn-Teller effect becomes the dominating factor, leading to charge ordering at a higher temperature than the antiferromagnetism. Here, there is much less sensitivity to magnetic fields. What is truly remarkable is that the range of $\langle r_A \rangle$ giving rise to such a wide

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spectrum of properties is only ~0.1 Å.

There are many curious features of the charge-ordered manganate systems. Thus, charge-ordering stripes are found in $La_{1-x}Ca_xMnO_3$ with $x > 0.5$ (*9*). In $Nd_{0.5}Ca_{0.5}MnO_3$, with its small $\langle r_A \rangle$, there is negligible change in volume at T_{co}, and the volume decreases continuously down to low temperatures. Charge localization also occurs at low temperatures, as indicated by the Mn bond valence sums (*10*). Even in the insulating phases, there would be Mn^{3+}-O-Mn^{4+} clusters and thermally activated hopping-inducing ferromagnetic interactions. Indeed, one of the problems with the charge-ordered manganates is the apparent presence of inhomogeneities in the composition of the A-site cations. How one can avoid such inhomogeneities is a question that merits further attention. Another important problem that needs further research is the effect of electric fields and radiation on the charge-ordered states. Structural studies of charge ordering and orbital ordering in manganates and the effect of magnetic fields on the charge-ordered states would also be of value.

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PLANT BIOLOGY

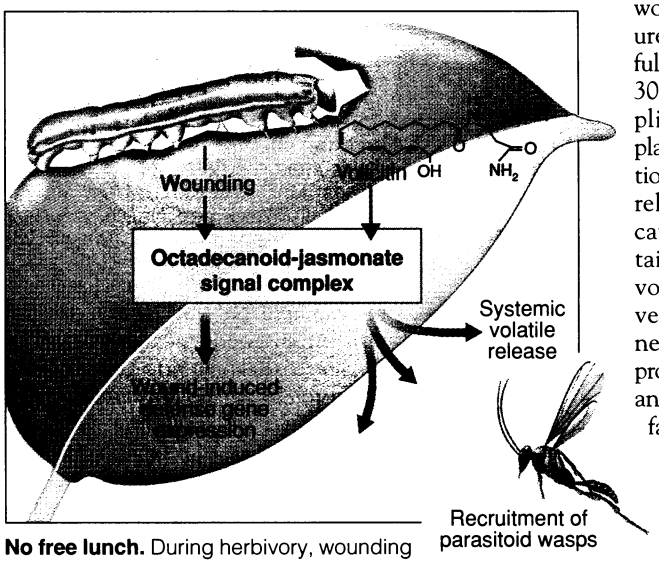
New Fatty Acid-Based Signals: A Lesson from the Plant World

Edward E. Farmer

Herbivorous insects and higher plants have been at war for well over 100 million years. During this time, the warring parties have evolved sophisticated strategies to eat or to avoid being eaten. Plants are equipped with an arsenal of constitutive and inducible defenses ranging from chemical poisons and feeding deterrents to proteins that can block the activity of the insects' digestive enzymes. Insects, on the other hand, can sometimes detoxify, sequester, or bypass these defenses. In the face of constant assault, how can plants augment their defenses? One answer is to recruit predators that attack the herbivores. During attack by insect herbivores, certain plants emit cocktails of volatile compounds that can attract other predatory or parasitic insects (*1–3*). In this issue on page 945, Alborn *et al.* (*4*) report an impressive advance in our knowledge of the trigger for the release of volatiles in herbivore-attacked plants that may have broader implications in our understanding of recognition phenomena in plant biology

When maize is attacked by beet armyworm caterpillars, the whole plant releases a cocktail of volatile terpenoids, which attracts parasitic wasps to the herbivore (*2*). Even a stealthy caterpillar hidden out of view is at risk when the host plant releases its volatile alarm signal. The specialized parasitoid wasps home in on the scent and deposit their eggs into the body of the herbivore in the biological equivalent of a time bomb: the emerging larvae devour their host.

What are the signals that cause plants to release parasitoid-attracting odors? In maize, mechanical damage alone is not sufficient to trigger scent release. Caterpillar regurgitant, however, applied to a mechanical wound causes release of the odor bouquet (*2*). Caterpillar-induced volatile production is an active process, at least in cotton, in which de novo synthesis of terpenoids is required for volatile release (*5*). Considered together, these data indicate the presence of a signal molecule in the herbivore oral secretions; the nature of this molecule has until now remained elusive. Alborn *et al.* (*4*) report the isolation and characterization of *N*-(17-hydroxylinolenoyl)-L-glutamine, or "volicitin," from the regurgitant of beet armyworm caterpillars fed on maize. This molecule triggers the release of the terpenoid cocktail that attracts the parasitic wasp *Cotesia marginiventris* to maize plants under attack by beet armyworm caterpillars (see figure). Volicitin is a powerful elicitor, and a little over 30 pmol of volicitin supplied to 2-week-old maize plants through the transpiration stream elicits volatile release (*5*). Beet armyworm caterpillar regurgitant contains about 20 pmol of volicitin per microliter, so very little saliva would be necessary to elicit terpenoid production (*5*). Volicitin joins an ever-growing family of fatty acid–based biological regulators and has structural features in common with molecules of very



No free lunch. During herbivory, wounding activates the systemic expression of defense genes through the octadecanoid signal pathway (*11*). In parallel, insect saliva containing chemical elicitors, such as volicitin (*4*), triggers the plant to release a bouquet of volatile compounds that attract parasitic or predatory insects to the herbivore. Volatile release stimulated by volicitin may also depend on the octadecanoid pathway, raising the possibility of cross talk between this molecule and the wound-induced expression of defense genes.

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