Structural Transformation Induced by Magnetic Field and "Colossal-Like" Magnetoresistance Response above 313 K in MnAs

J. Mira,[1] F. Rivadulla,[2] J. Rivas,[1] A. Fondado,[1] T. Guidi,[3] R. Caciuffo,[3] F. Carsughi,[3] P. G. Radaelli,[4] and J. B. Goodenough[2]

[1]*Departamento de Física Aplicada, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain*
[2]*Texas Materials Institute, ETC 9.102, The University of Texas at Austin, Austin, Texas 78712*
[3]*Istituto Nazionale per la Fisica della Materia, Dipartimento di Fisica, Universitá di Ancona, I-60131 Ancona, Italy*
[4]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, United Kingdom and Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom*

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MnAs exhibits a first-order phase transition from a ferromagnetic, high-spin metal hexagonal phase to a paramagnetic, lower-spin insulator orthorhombic phase at $T_C = 313$ K. Here, we report the results of neutron diffraction experiments showing that an external magnetic field, B, stabilizes the hexagonal phase above T_C. The phase transformation is reversible and constitutes the first demonstration of a bond-breaking transition induced by a magnetic field. The field-induced phase transition is accompanied by an enhanced magnetoresistance of about 17% at 310 K. The phenomenon appears to be similar to that of the colossal magnetoresistance response observed in the Mg perovskite family.

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MnAs is a commercially available material, intensively studied, both theoretically and experimentally, since the beginning of the last century. Interest in this compound could come up again as a consequence of new ideas and conjectures formulated during the last decade in connection with the study of the colossal magnetoresistance (CMR) response in Mn perovskites [1]. Among these ideas is the invocation of a phase separation scenario for CMR manganese oxides and related materials [2] that might be of particular relevance in systems, like MnAs, where first-order phase transitions occur.

To our knowledge, MnAs was first studied by Heusler [3], and later by Hilpert and Dieckmann [4], who discovered that the compound is ferromagnetic with a Curie temperature of $T_C \simeq 313$ K. Serres [5] and Guillaud [6] found that a metal-insulator transition occurs at T_C. Some years later, Willis and Rooksby [7] measured a large (1.86%) discontinuous density change at T_C. Bean and Rodbell [8] used the volume change to describe the first-order loss of magnetization, which takes place with a latent heat of 1.79 cal/K [9], in terms of a volume-dependent exchange interaction. De Blois and Rodbell [10] explored the change in T_C with pressure to $P = 1$ kbar in fields $0 < B < 11$ T. A second-order phase transition, with no volume change, was detected by calorimetric measurements at $T_t = 399$ K [11]. Between T_C and T_t, the magnetic susceptibility increases with temperature [5,12], transforming to a Curie-Weiss law above T_t. X-ray diffraction studies[13] revealed a change in the crystallographic arrangement at the first-order transition point, from the NiAs-type ($B8_1$) hexagonal structure to the MnP-type ($B31$) orthorhombic one. The orthorhombic distortion decreases with increasing temperature and the hexagonal $B8_1$ structure reappears above T_t. It was soon recognized that a crossover from high to low-spin states on the manganese site could occur on going from the $B8_1$ to the $B31$ structure [14]. Studies of the influence of higher hydrostatic pressure on MnAs led to a modification of the Bean-Rodbell theory [11,15]. The spin-state instability appears to be responsible for a giant magnetoelastic response reported recently by Chernenko *et al.* [16].

Our neutron diffraction study of the stability of the orthorhombic $B31$ phase of MnAs in an applied magnetic field B was performed on the D2B high-resolution, angle-dispersive powder diffractometer of the Institute Laue-Langevin (ILL) in Grenoble, France, and on the POLARIS time-of-flight diffractometer of the ISIS facility at the Rutherford-Appleton Laboratory, Oxfordshire, U.K. Two kinds of polycrystalline samples were measured for this work. A commercial one provided by Western Inorganics was investigated at the ILL. It was contaminated by MnO impurities and contained traces of unidentified phases. The MnO was removed by a digestion of the MnAs in hot HCl. After this process the sample was washed with water and dried. X-ray analysis confirmed that monoxide was practically removed. This sample was measured at ISIS. The two experiments have given consistent results and, in the following, we will present only data recorded on POLARIS. For measurements on this instrument, 5 g of MnAs were packed in a cylindric vanadium holder, 40 mm in height, and inserted into a 5.5 T Oxford-Instrument superconducting cryomagnet. Two temperature probes were used, one sealed at the top of the sample can, and the other at the bottom. Also, the commercial sample as well as another synthesized in our laboratory by solid-vapor reaction were used for magnetoresistance (MR) studies. For the

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latter, Mn and As powder (− 325 mesh) were sealed in evacuated ($P \simeq 10^{-5}$ torr.) quartz tubes and heated at 823 K for 24 h. This process was repeated several times with intermediate grindings to obtain a pure, single phase compound. For MR measurements the powder was cold-press at $\simeq 160$ ton/cm^2 and sintered again, which practically eliminated any grain boundary contributions to MR.

At room temperature, below $T_C = 313$ K, the diffraction pattern was that of the hexagonal $B8_1$ phase (space group $P6_3/mmc$) with lattice parameters [$a = 3.7187(5)$ Å, $c = 5.7024(5)$ Å at $T = 300$ K] in agreement with those reported by Willis and Rooksby [7]. Reflections belonging to the orthorhombic $B31$ structure described by Wilson and Kasper [13] appeared above T_C. Figure 1 shows the evolution of the diffraction pattern as the temperature is increased from 312 to 317 K. The hexagonal and the orthorhombic phases coexist between 313 and 315 K, while the whole sample is in the orthorhombic phase at 317 K.

The sample was then heated at 321 K, and equilibrated at that temperature for 2 h in zero field. The magnetic field was then increased at regular steps up to 5.5 T and the diffractograms recorded at each step. The results are reported in Fig. 2. It is readily apparent that the diffraction profile is substantially modified as B increases above 3.5 T, and that the hexagonal phase is fully restored at $B = 5$ T. Indeed, diffractograms o (321 K, $B = 5.5$ T) and p (300 K, $B = 0$) in Fig. 2 are practically indistinguishable. The field-induced transition is clearly visible in the lattice spacing range from 2.75 to 2.9 Å, shown in Fig. 3. The unresolved (111)-(102) doublet of the orthorhombic phase at about 2.78 Å progressively disappears as the (101) hexagonal peak at 2.81 Å grows in intensity. The extent of the orthorhombic distortion decreases continuously as B increases, nearly vanishing by $B = 5.0$ T. The magnetic field evolution of the diffraction pattern has also been measured at 319 and 318 K. With decreasing temperature, the phase transformation occurs at smaller values of the magnetic field (2.5–4.0 T at 318 K, 3.0–4.5 T at 319 K).

The neutron diffraction data do not show a sharp transition, but rather the coexistence of two phases with the growth of the ferromagnetic phase at the expense of the paramagnetic $B31$ phase as B increases. Growth of the ferromagnetic phase is possible because the $B31$ phase is derived from the $B8_1$ phase by a cooperative displacement of pairs of $[1, -1, 0]$ rows toward one another to form stronger Mn-Mn bonds, across shared octahedral-site edges in zigzag chains within the basal planes. These displacements also create shorter Mn-As bonds, which

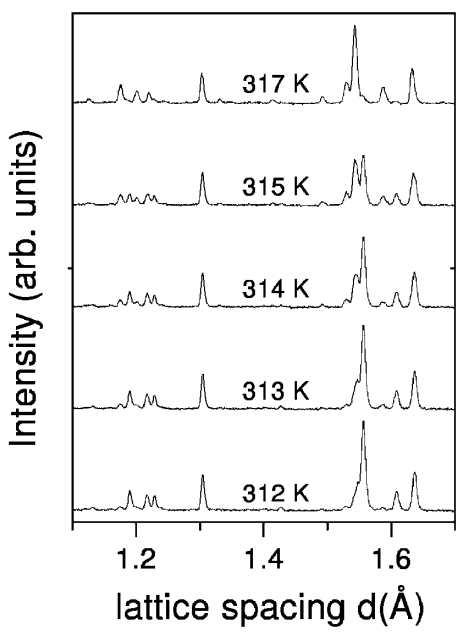

FIG. 1. Temperature dependence of the MnAs diffractogram in a selected d spacing range. The hexagonal-orthorhombic transition starts at 313 K and is completed at 317 K.

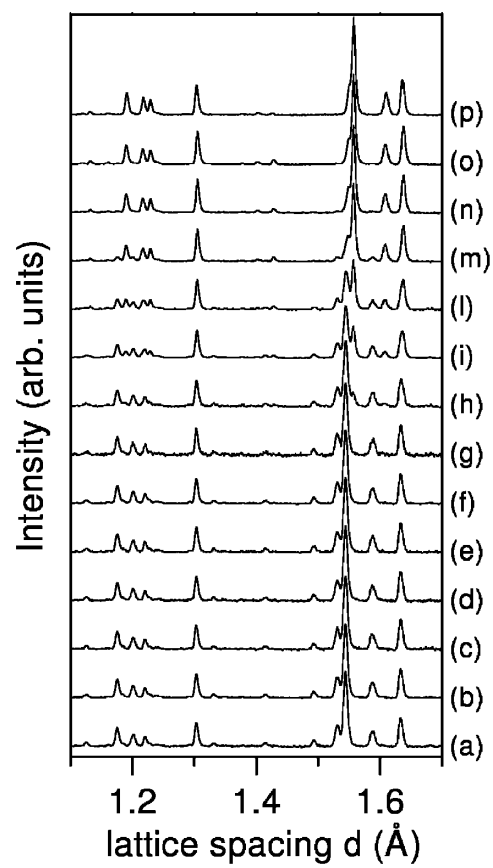

FIG. 2. Magnetic field dependence of a selected region of the diffraction pattern recorded at 321 K, showing the evolution from the orthogonal to the hexagonal form of MnAs: (a) $B = 0$ T; (b) $B = 0.50$ T; (c) $B = 1.00$ T; (d) $B = 1.50$ T; (e) $B = 2.00$ T; (f) $B = 2.75$ T; (g) $B = 3.00$ T; (h) $B = 3.50$ T; (i) $B = 3.75$ T; (l) $B = 4.00$ T; (m) $B = 4.50$ T; (n) $B = 5.00$ T; (o) $B = 5.50$ T; (p) $T = 300$ K, $B = 0$ T.

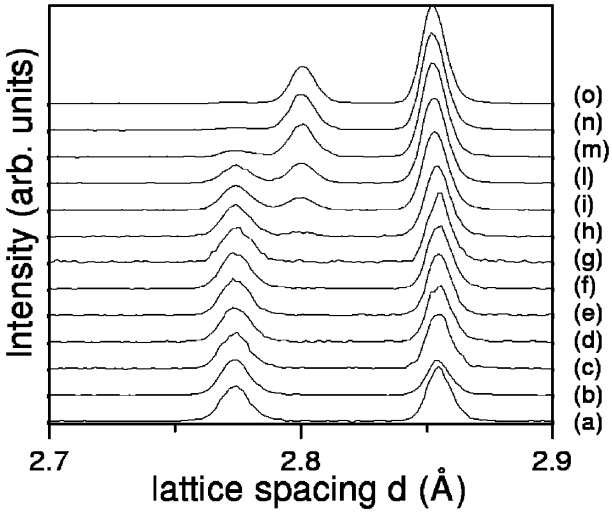

FIG. 3. Magnetic field dependence of a selected region of the diffraction pattern recorded at 321 K, showing the evolution from the orthogonal to the hexagonal form of MnAs: (a) $B = 0$ T; (b) $B = 0.50$ T; (c) $B = 1.00$ T; (d) $B = 1.50$ T; (e) $B = 2.00$ T; (f) $B = 2.75$ T; (g) $B = 3.00$ T; (h) $B = 3.50$ T; (i) $B = 3.75$ T; (l) $B = 4.00$ T; (m) $B = 4.50$ T; (n) $B = 5.00$ T; (o) $B = 5.50$ T.

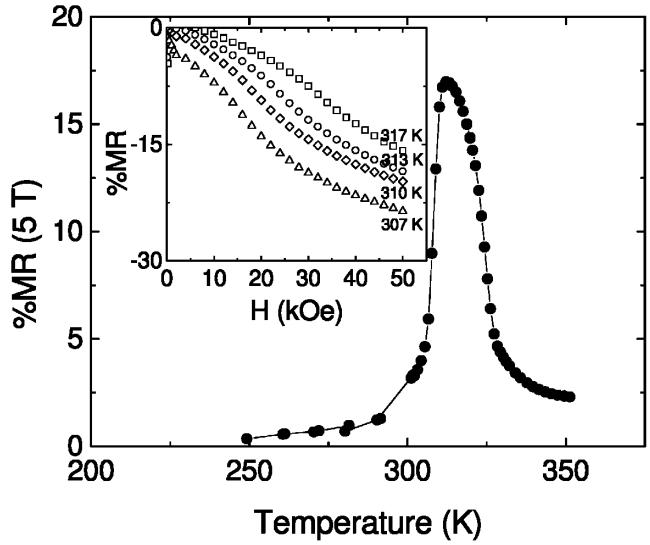

FIG. 4. Magnetoresistance $\{MR = [\rho(0) - \rho(5\ \mathrm{T})]/\rho(0) \times 100\}$ versus temperature of MnAs. Inset: MR vs H.

raises the antibonding states that σ bond to the As atoms and triggers the transition to a low-spin state [15].

Extrapolation of the Brillouin temperature dependence of the magnetization of the $B8_1$ phase to above the first-order transition at T_C gives a fictitious Curie temperature $T_C^* = 388$ K. Since an applied magnetic field B stabilizes the high-spin, ferromagnetic phase relative to the $B31$ paramagnetic phase, a global insulator-metal $B31$-$B8_1$ transition might be induced by B in the interval $T_C < T < T_C^*$. Alternatively, if $B8_1$ regions exist within a $B31$ matrix in the interval $T_C < T < T_t$, we can expect that below T_C^* the ferromagnetic $B8_1$ regions will grow in a magnetic field at the expense of the paramagnetic $B31$ matrix to beyond the percolation threshold. In either case, a CMR would occur between T_C and T_C^*. If the B field induces a global $B31$–$B8_1$ transition, it would give a CMR analogous to that found, for example, at the metamagnetic transition of the charge and orbital-ordered CE phase of the perovskite $Nd_{0.5}Sr_{0.5}MnO_3$ [17]. If, on the other hand, the magnetic field nucleates and/or grows the $B8_1$ phase, it would give a CMR phenomenon analogous, for example, to that of the perovskite system $(La_{0.7-x}Pr_x Ca_{0.3})MnO_3$ [18]. However, whereas the CMR occurs in the manganese oxides at too low a temperature to be technically practical, it would occur in MnAs a little above room temperature and could easily be adjusted to operate at room temperature by small compositional changes.

Figure 4 shows the enhanced magnetoresistance response of MnAs measured in the predicted temperature range, $T_C < T < T_C^*$. Almost the same results were obtained for both samples used in this study. Although the absolute value of the magnetoresistance is not as large as in other compounds like $La_{2/3}Ca_{1/3}MnO_3$ [19], we call it CMR-like to highlight the common origin with that in the manganites. It is clear that the origin of this MR effect is intrinsic and not due to an intergranular process in a material with a high-spin polarization. This is reflected (besides the independence of the result on sample synthesis) in an almost straight field dependence of the MR (see the inset of Fig. 4) and the almost temperature independent MR below the peak centered at T_C. Analogies between the behavior of MnAs in a magnetic field above T_C and that of the manganese-oxide perovskites are noteworthy. In the manganese perovskites, the σ-bonding d electron of a high-spin octahedral-site Mn(III) ion occupies a twofold-degenerate pair of e orbitals. This e orbital degeneracy is removed by a local distortion of the $MnO_{6/2}$ octahedron; and at lower temperatures and high Mn(III) concentrations, the local distortions are ordered cooperatively so as to minimize the associated elastic energy. A recent study of $LaMn_{1-x}Ga_xO_3$ [20] has shown that in this single-valent system, dilution of the Mn(III) atoms suppresses the orbital ordering in local ferromagnetic regions; a vibronic superexchange is ferromagnetic whereas the orbitally ordered matrix is antiferromagnetic. In this system, application of B disorders the orbital order of the matrix to transform a spin glass to a ferromagnet [20]. In the mixed-valent perovskite system $La_{1-x}Sr_xMnO_3$, an orthorhombic-rhombohedral structural phase transition is induced by an external magnetic field for $x = 0.17$ [21]; this transition involves a change from $[1, -1, 0]$ to $[1, 1, 1]$ of the axis of cooperative rotation of the $MnO_{6/2}$ octahedra. A crossover from localized to itinerant behavior of the σ-bonding e electrons occurs in the compositional interval $0.1 \leq x \leq 0.17$ [22]. In this interval, hole-rich

ferromagnetic regions are segregated from a hole-poor paramagnetic matrix in the paramagnetic temperature range $T_C < T \leq 300$ K by cooperative oxygen displacements. The hole-rich regions are mobile, and they grow in a B to beyond a percolation threshold by $B = 5$ T to give the CMR-like phenomenon. In the interval $0.1 \leq x \leq 0.15$, the transition at T_C is first order, and in a narrow temperature range $T_{OO} < T < T_C$, the orbitals undergo a rearrangement to another type of order below T_{OO}. Near $x = 0.1$, the interval $T_{OO} < T < T_C$ narrows, and the matrix remains orbitally ordered in zero magnetic field to give spin-glass behavior typical of ferromagnetic clusters having a T_C greater than the Néel temperature of the matrix. However, the orbitals of the matrix become disordered in a modest B to give ferromagnetic order below a T_C. Recently, Mira *et al.* [23] observed a second-order transition at a temperature $T^* > T_C$ in the compositional interval where they had noted a first-order transition at T_C [24]. In the range $T_C < T < T^*$, a non–Curie-Weiss paramagnetism has been found by de Teresa *et al.* [25], similar to the behavior of MnAs in the range $T_C < T < T_t$ [5,6]. Moreo *et al.* [26] have made a computational study to argue that in the mixed-valent manganese-oxide perovskites, hole-rich clusters that are metallic and ferromagnetic coexist with a paramagnetic, hole-poor insulating matrix; the ferromagnetic clusters grow in a magnetic field B. Goodenough [27] has invoked the virial theorem to make the same deduction for the manganese-oxide perovskites at the crossover from localized to itinerant behavior of the σ-bonding electrons. However, MnAs is single-valent, so the analogy with $LaMn_{1-x}Ga_xO_3$ is more appropriate even though this perovskite remains insulating in the ferromagnetic phase. In MnAs, the basal-plane orbitals on the Mn atoms are half-filled, and the electrons approach the crossover from localized to itinerant electronic behavior. In the paramagnetic $B31$ phase, the Mn atoms become displaced below T_t so as to form stronger Mn-Mn bonds in the zigzag chains and weaker Mn-Mn bonds between the chains. These displacements not only order the Mn-As bonding so as to induce the low-spin state, but they also represent an ordering of the inplane Mn-Mn bonds that change the translational symmetry so as to split the basal-plane band at the Fermi energy. Ferromagnetic interactions by the other d electrons are dominant, but these interactions are weakened by the transition to the low-spin state, which reduces the Mn-Mn separation and strengthens the inplane Mn-Mn bonding. Since no bonding occurs between half-filled orbitals with parallel spins, stabilization of the high-spin ferromagnetic $B8_1$ phase suppresses inplane Mn-Mn bonding and increases the inplane Mn-Mn separation. Stabilization of the ferromagnetic phase in a B with removal of the inplane Mn-Mn bonding is to be compared with suppression by a B of the orbital ordering at the Mn(III) ions in $LaMn_{1-x}Ga_xO_3$. This is the first crystallographic transition induced by a magnetic field that involves breaking of metal-metal bonds rather than orbital disorder.

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