MnAs exhibits a first-order phase transition from a ferromagnetic, high-spin metal NiAs-type hexagonal phase to a paramagnetic, lower-spin insulator MnP-type 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 metallic phase above \( T_C \). The phase transition is reversible and constitutes the first demonstration of a bond-breaking transition induced by a magnetic field. At 322 K the hexagonal structure is restored for \( B > 4 \) tesla. The field-induced phase transition is accompanied by an enhanced magnetoresistance of about 17% at 310 K. We discuss the origin of this phenomenon, which appears to be similar to that of the colossal magnetoresistance response observed in some members of the manganese perovskite family.

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 \( T_C \approx 313 \) K. Serres \(^5\) and Guillaud \(^6\) found that a metal-insulator transition occurs at \( T_C \). The abrupt loss of magnetization at \( T_C \) led Meyer and Taglang \(^7\) to assume a ferromagnetic-antiferromagnetic transition at \( T_C \). However, a neutron-diffraction study by Bacon and Street \(^8\) showed that this was not the case. At the same time, Willis and Roosby \(^9\) measured a large (1.86%) discontinuous density change at \( T_C \) that had been previously detected by Smits, Gerding, and Ver Mast \(^6\). Bean and Rodbell \(^10\) used the volume change to describe the first-order loss of magnetization, which takes place with a latent heat of 1.79 cal/K \(^1\), in terms of a volume-dependent exchange interaction. De Blois and Rodbell \(^11\) 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 \( T_I = 399 \) K \(^1\). Between \( T_C \) and \( T_I \), the magnetic susceptibility increases with temperature \(^1\), transforming to a Curie-Weiss law above \( T_I \). 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 \( B31 \) structure reappears above \( T_I \). It was soon recognized that a cross-over from high to low spin states on the manganese site could occur on going from the \( B8_1 \) to the \( B31 \) structure \(^14\) (Fig. 1). This conjecture led to a study of the \( \text{MnAs}_{1-x}\text{P}_x \) and \( \text{MnAs}_{1-x}\text{Sb}_x \) systems that demonstrated the spin transition \(^20\). Studies of the influence of higher hydrostatic pressure on MnAs led to a modification of the Bean-Rodbell theory \(^16\), \(^21\). The spin-state instability appears to be responsible for a giant magnetoelas tic response reported recently by Chernenko et al. \(^22\).

Our neutron diffraction study of the stability of the orthorhombic \( B31 \) phase of MnAs in an applied magnetic field \( B \) was performed on the high-resolution powder diffractometer D2B of the Institute Laue-Langevin in Grenoble, France. Two kinds of polycrystalline samples were measured for this work, namely a commercial one provided by Western Inorganics and another synthesized in our laboratory by solid-vapor reaction. Mn and As powder (-325 mesh) were sealed in evacuated (\( P \approx 10^{-5} \) torr) quartz tubes and heated at 823 K for 24 hours. This process was repeated several times with intermediate grindings to obtain the pure compound. In the commercial sample we detected the presence of MnO impurities, but this has no influence on the structural results here discussed. For neutron diffraction experiments, two grams of MnAs were packed in a cylindrical vanadium holder and inserted into a 5-tesla superconducting cryomagnet. The instrument is equipped with 64 collimated \(^3\)He detectors spaced at 2.5 intervals and covering a \( 2\theta \) angular range from 5° to 165°. A complete diffraction pattern was obtained by moving the detector bank 100
times in angular steps of 0.025°. Data have been collected with incident neutrons of wavelength \(\lambda = 1.5943(1)\ A\) selected by Ge (3 3 5) monochromators.

At room temperature, below \(T_C = 313\ K\), the diffraction pattern was that of the hexagonal \(B8_1\) phase with lattice parameters in agreement with those reported by Willis and Rooksby \[11\]. Reflections belonging to the orthorhombic \(B31\) structure described by Wilson and Kasper \[13\] appeared above \(T_C\). As shown in Fig. 3, the differences between the diffraction patterns measured in zero field at 300 K and 322 K are readily apparent. However, with the sample held at 322 K, the application of a magnetic field \(B\) modifies substantially the diffraction profile. For a \(B = 5\ T\), the diffraction pattern at 322 K is essentially the same as that at 300 K in zero applied field. The hexagonal \(B8_1\) structure is clearly restored fully by the application of a \(B = 5\ T\). As is clear from Fig. 3, the extent of the orthorhombic distortion decreases continuously as \(B\) increases, nearly vanishing by \(B = 4\ T\). These data do not show a sharp transition, but rather a continuous transition at a temperature to be technically practical, it would occur in \(B = 5\ T\) to give the \(B31\) phase with the growth of the ferromagnetic phase at the expense of the paramagnetic \(B8_1\) phase as \(B\) increases. Growth of the ferromagnetic phase is possible because the \(B31\) phase is derived from the \(B8_1\) phase by a co-operative displacement of pairs of \(1, -1, 0\) rows toward one another to form stronger Mn-Mn bonds, across shared octahedral-site edges in zig-zag chains within the basal planes. These displacements also create shorter Mn-As bonds, which raises the antibonding states that \(\sigma\)-bond to the As atoms and triggers the transition to a low-spin state \[2\].

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 \(T^{\ast}_C = 388\ K\). 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 \(T_C < T < T^{\ast}_C\). Alternatively, if \(B8_1\) regions exist within a \(B31\) matrix in the interval \(T_C < T < T_i\), we can expect that below \(T_i\) 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 \(T^{\ast}_C\). 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 \(Nd_{0.5}Sr_{0.5}MnO_3\) \[2\]. 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 \((La_{0.7-x}Pr_xCa_{0.3})MnO_3\) \[2\]. 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.

Fig. 4 shows the enhanced magnetoresistance response of MnAs measured in the predicted temperature range, \(T_C < T < T^{\ast}_C\). 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 \(La_{2/3}Ca_{1/3}MnO_3\) \[25\], we call it a CMR to highlight the common origin with that in the manganites. 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 \(\sigma\)-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$_x$O$_3$ \[26\] 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 ferromagnetic \[27\]. In the mixed-valent perovskite system La$_{1-x}$Sr$_x$MnO$_3$, an orthorhombic-rhombohedral structural phase transition is induced by an external magnetic field for \(x = 0.17\) \[27\]; 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 \(\sigma\)-bonding \(e\)-electrons occurs in the compositional interval \(0.1 \leq x \leq 0.17\) \[28\]. In this interval, hole-rich ferromagnetic regions are segregated from a hole-poor paramagnetic matrix in the paramagnetic temperature range \(T_C < T < 300\ K\) 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 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 \(T_C\). Recently, Mira et al. \[24\] have 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. \[31\], similar to the behavior of MnAs in the range \(T_C < T < T_i\). Moreo et al. \[22\] 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 [32] has invoked the virial theorem to make the same deduction for the manganese-oxide perovskites at the crossover from localized to itinerant behavior. However, MnAs is single-valent, so the analogy with LaMn$_{1-x}$Ga$_x$O$_3$ 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 electron approach the crossover from localized to itinerant electronic behavior. In the paramagnetic $B31$ phase, the Mn atoms become displaced below $T_c$ 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 in-plane Mn-Mn bonds that changes 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 in-plane Mn-Mn bonding. Since no bonding occurs between half-filled orbitals with parallel spins, stabilization of the high-spin ferromagnetic $B8_1$ phase suppresses in-plane Mn-Mn bonding and increases the in-plane Mn-Mn separation. Stabilization of the ferromagnetic phase in a B with removal of the in-plane 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$_x$O$_3$. This is the first crystallographic transition induced by a magnetic field that involves breaking of metal-metal bonds rather than orbital disorder.

We are pleased to thank the valuable aid provided by A. Hewat and the ILL technical staff during the neutron diffraction experiment and the operation of the cryomagnet in unusual conditions and J. S. Zhou, from the Texas Materials Institute for his help with the magnetoresistance measurements. F. R. thanks the Fulbright foundation and MECD from Spain for a postdoctoral fellowship. We also acknowledge the DGI of the Ministry of Science and Technology of Spain for financial support under project MAT2001-3749 JBG thanks the NSF for financial support.

[1] J. M. D. Coey, M. Viret, and S. von Molnár, Adv. Phys. 48, 167 (1999).
[2] A. Moreo, S. Yunoki, and E. Dagotto, Science 283, 2034 (1999).
[3] F. Heusler, Z. Angew. Chem. 17, 260 (1904).
[4] S. Hilpert and T. Dieckmann, Ber. Deut. Chem. Ges. 44, 2378 (1911).
[5] S. Hilpert and T. Dieckmann, Ber. Deut. Chem. Ges. 44, 2831 (1911).
[6] S. Hilpert, T. Dieckmann, and E. Colver-Glauert, Trans. Faraday Soc. 8, 207 (1912).
[7] A. Serres, J. Phys. Radium 8, 146 (1947).
[8] C. Guillaud, J. Phys. Radium 12, 223 (1951).
[9] A. J. P. Meyer and P. Taglang, J. Phys. Radium 12, 635 (1951).
[10] G. E. Bacon and R. Street, Nature 175, 518 (1955).
[11] B. T. M. Willis and H. P. Rooksby, Proc. Phys. Soc. (London) B67, 290 (1954).
[12] A. Smits, H. Gerdig, and F. Ver Mast, Z. Physik. Chem. Bodenstein Festband (Leipzig), 357 (1931).
[13] C. P. Bean and D. S. Rodbell, Phys. Rev. 126, 104 (1962).
[14] L. F. Bates, Proc. Roy. Soc. (London) A117, 680 (1928).
[15] R. W. de Blois and D. S. Rodbell, Phys. Rev. 130, 1347 (1963).
[16] M. Menyuk, J. A. Kafalas, K. Dwight, and J. B. Goodenough, Phys. Rev. 177, 942 (1969).
[17] F. Bates, Phil. Mag. 8, 714 (1929).
[18] R. H. Wilson and J. S. Kasper, Acta Cryst. 17, 95 (1964).
[19] J. B. Goodenough, Influence of metal-metal bonding on structures derived from NiAs structure, MIT technical report, No. 345 (1964), unpublished.
[20] J. B. Goodenough, D. H. Ridley, and W. A. Newman, Proceedings of the International Conference on Magnetism, Nottingham, 1964 (The Institute of Physics and the Physical Society, London, 1965).
[21] J. B. Goodenough and J. A. Kafalas, Phys. Rev. 157, 389 (1967).
[22] V. A. Chernenko, L. Wee, P. G., McCormick, and R. Street, J. Appl. Phys. 85, 7833 (1999).
[23] S. Shimomura, K. Tajima, N. Wakabayashi, H. Kuwahara, and Y. Tokura, J. Phys. Soc. Japan 68, 1943 (1999).
[24] H. Y. Hwang, S.-W. Cheong, P. G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. 75, 914 (1995).
[25] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, Science 264, 413 (1994).
[26] J. S. Zhou, H. Q. Yin, and J. B. Goodenough, Phys. Rev. B 63, 184423 (2001).
[27] T. Nishihara, Y. Morimoto, Y. Tomioka, T. Arima, and Y. Tokura, Nature 373, 407 (1995).
[28] G. L. Liu, J. S. Zhou, and J. B. Goodenough, Phys. Rev. B 64, 144414 (2001).
[29] J. Mira, J. Rivas, L. E. Hueso, F. Rivadulla, M. A. López Quintela, M. A. Señarís Rodríguez, and C. A. Ramos, Phys. Rev. B 65, 024418 (2001).
[30] J. Mira, J. Rivas, F. Rivadulla, C. Vázquez Vázquez, and M. A. López Quintela, Phys. Rev. B 60, 2998 (1999).
[31] J. M. de Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. García, A. del Moral, and Z. Arnold, Nature 386, 256 (1997).
[32] A. Moreo, M. Mayr, A. Feiguin, S. Yunoki, and E. Dagotto, Phys. Rev. Lett. 84, 5568 (2000).
[33] J. B. Goodenough, Aust. J. Phys. 52, 155 (1999).
FIG. 1: The orthorhombic unit cell of the $B31$ form of MnAs in relation to the hexagonal $B8_1$ type cell. Mn (white circles) and As (black circles) atoms are in the 4c special positions of the Pnma space group, $(x,1/4,z)$, with $x = -0.005$ and $z = 0.223$ for Mn, $x = 0.275$ and $z = -0.082$ for As.

FIG. 2: Selected regions of the diffraction patterns recorded at 27 °C with no field (circles), at 49 °C with no field (squares) and at 49 °C with an applied field of 5 tesla (triangles).
FIG. 3: Magnetic field dependence of a selected region of the diffraction pattern recorded at 322 K, showing the evolution from the orthogonal to the hexagonal form of MnAs.

FIG. 4: Magnetoresistance (MR=[ρ(0)-ρ(5T)/ ρ(0)] x 100) versus temperature of MnAs and magnetisation measured at 0.1 T in zero-field-cooling conditions.