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Neutron diffraction in $\mathrm{Ho(Mn_{0.9}Al_{0.1})_2}$ under pressure up to 7.8 GPa: Long-range magnetic order induced by pressure in a frustrated system

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In $\mathrm{Ho(Mn_{0.9}Al_{0.1})_2}$, applying pressure results in the occurrence of several magnetic phase transitions. The disordered phase disappears and long-range ordered phases are stabilized, as the pressure suppresses the frustrated Mn spins. A canted antiferromagnetic structure appears initially, then transforms into a ferromagnetic structure. The suppression of frustration is associated with a change in the delicate energy balance of the spin interactions, as the rare earth magnetism becomes dominant. The changes in the magnetic order are interpreted by a change in the nature of Mn magnetism, from a localized to an induced and finally to a nonmagnetic state.

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Topological frustration of a magnetic lattice yields many interesting phenomena, such as spin glass, spin liquid or spin ice states, which have recently attracted great attention. The inability of a magnetic system to reach a long range ordered state comes from the geometry of the lattice,which does not allow spin interactions to be satisfied.[1–3] In the Laves compounds $R\mathrm{Mn}_2$, where R is a rare earth metal, the pyrochlorelike Mn lattice is topologically frustrated with antiferromagnetic nearest neighbor exchange interactions, whereas the diamondlike lattice of the rare earth metal is not frustrated.[4] The interplay between R and Mn magnetism can yield complex magnetic structures, as observed in $\mathrm{TbMn_2}$ (Ref. 5) and $\mathrm{GdMn_2}$.[6] Moreover, the Mn magnetism is unstable, depending on the interatomic distance between neighboring Mn pairs, with a threshold of instability at a critical distance.[7] When Mn moments lose their intrinsic nature, the R-Mn interactions can stabilize Mn magnetism by inducing moments on some Mn sites, releasing the frustration at the same time.[8]

Since the variation of interatomic distances is a key parameter of their magnetism, the $R\mathrm{Mn}_2$ compounds are very sensitive to a chemical or applied pressure. Substitution on the R and Mn sites or even chemical doping of interstitial sites have been widely used to vary Mn distances in these compounds.[9] However, chemical substitution also produces unwanted effects such as dilution of the magnetic lattice and irregular local environments. In a system with topological frustration, the subsequent change of the frustration could be huge even at very low defect concentration, as first noticed by Villain[10] in the 1980s. An applied pressure is obviously the most direct and clean way to vary interatomic distances. Until now, neutron studies were limited to small pressures of few kbars. They studied the evolution of magnetic structures nearby the instability threshold of $\mathrm{YMn_2}$, $\mathrm{TbMn_2}$, and their alloys.[11,12] In these cases, a pressure of a few kbars was enough to suppress intrinsic Mn magnetism, as also shown by magnetization.[13] In recent years Mössbauer, NQR/NMR, resistivity, and thermal expansion measurements have been performed under higher pressures, in the range 0–40 kbars in $\mathrm{YMn_2}$ and $\mathrm{GdMn_2}$.[14–18] They suggested unusual pressure effects, such as a change in the nature of the spin fluctuations or a decoupling of R and Mn magnetic lattices. However, only neutron diffraction measurements under pressure could tell how pressure modifies the magnetic structure.

$\mathrm{HoMn_2}$ is situated just below the instability threshold, and Mn moments are induced by Ho ones.[8] Magnetic Mn1 planes alternate with nonmagnetic Mn2 ones, in a canted antiferromagnetic structure. Mn1 planes are hexagonal, involving second neighbors Mn pairs only, and induced Mn moments of about $0.6\mu_B$. Mn2 planes are Kagomé like, with strong topological frustration. In these planes the Ho molecular fields partially cancel. Al substitution on Mn sites yields a lattice expansion and a strong change of the magnetic order.[19] Short range antiferromagnetic correlations are stabilized, coexisting with incommensurate and ferromagnetic orders at low Al content.

We have performed high pressure neutron diffraction in a $\mathrm{Ho(Mn_{0.9}Al_{0.1})_2}$ sample under much higher pressures than in usual neutron measurements. The large pressures (up to 78 kbars or 7.8 GPa) allow us to discriminate the effects of applied and chemical pressure. Moreover, the decrease of interatomic distances induced by pressure changes the nature of the Mn moment, modifies the magnetic structure and even induces a long range ferromagnetic order at very high pressure.

Measurements were performed on the powder diffractometer G61 of the LLB at the Orphée reactor, with an incident wavelength 4.74 Å. The spectrometer was modified for high pressure studies which require very small sample volumes (down to 0.3 mm^3 in the present case). Focusing devices[20] were used to increase the neutron flux, together with careful shielding of the sample environment. The sample was loaded in a sapphire anvil cell[21] inserted in a cryostat modified to decrease the background. The temperature varied between 1.5 and 300 K.

Figure 1 shows neutron diffraction patterns measured at 1.5 K for several pressures. Pattern measured in the paramagnetic range were subtracted to isolate the magnetic signals. At ambient pressure,[19] the Mn-Mn distance of 2.67(1) Å is just in the range of the instability threshold

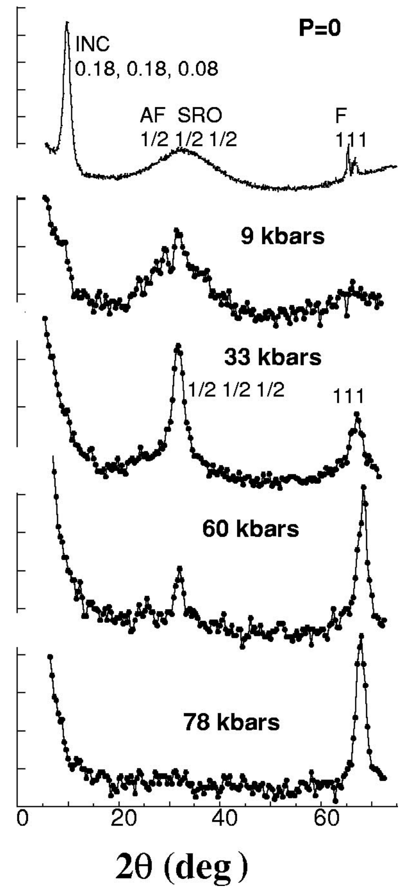

FIG. 1. Magnetic neutron diffraction spectra at 1.5 K for several pressures in $Ho(Mn_{0.9}Al_{0.1})_2$.

(2.67 Å from Ref. 26). Under applied pressure, it decreases down to 2.60(1) Å at 7.8 GPa, allowing one to go well below the instability threshold. The volume of the unit cell decreases about 8% at 7.8 GPa, without any anomaly versus pressure (Fig. 2). The ambient pressure pattern shows a well defined satellite at low angles and a diffuse peak at higher angles. From Ref. 19, they are respectively attributed to an incommensurate structure with wave vector $\mathbf{k} = [0.18,0.18,0.08]$, and to short range antiferromagnetic correlations extending over about 25 Å. By applying pressure, drastic changes occur in the magnetic scattering. A very low pressure ($P<0.9$ GPa) suppresses the incommensurate satellite seen at ambient pressure. The short range order (SRO) disappears more gradually, above 4 GPa. Instead, narrow magnetic Bragg peaks start to grow both at the (1/2 1/2 1/2) and (1 1 1) peak position, resulting from the onset of long range order (LRO). When pressure increases further, the (1/2 1/2 1/2) Bragg peak starts to decrease and disappears at the highest pressure (7.8 GPa), where only a very strong Bragg peak remains at the (1 1 1) position.

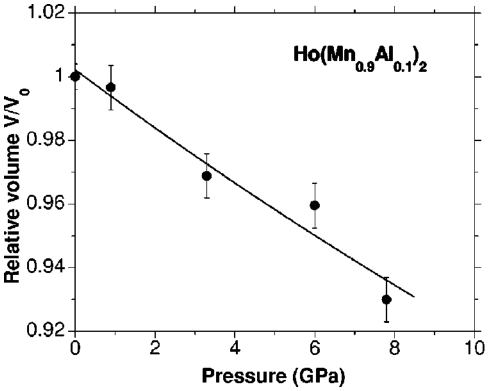

FIG. 2. Volume of the unit cell in relative units versus pressure. The solid line is a fit of the data by the Birch equation, yielding a bulk modulus $B_0 = 106.6$ GPa, and its derivative $B_1 = 2.0$.

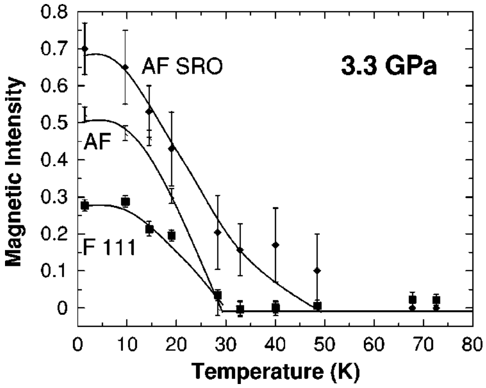

FIG. 3. Integrated intensities of the 111 and 1/2 1/2 1/2 magnetic Bragg peaks, and of the diffuse magnetic peak of the SRO phase *versus* temperature at 3.3 GPa.

The LRO phase stabilized at intermediate pressures (3–7 GPa) shows both antiferromagnetic (AF) and ferromagnetic (F) contributions, at (1/2 1/2 1/2) and (1 1 1) positions respectively. It could be attributed to the canted structure observed in $HoMn_2$, where Mn magnetism is induced by the Ho moments.[8] The single magnetic peak observed at 7.8 GPa is attributed to a simple ferromagnetic order, expected to occur between Ho moments if the Mn ones completely collapse. At 7.8 GPa, a calibration of the magnetic to the structural intensity of the (1 1 1) peak yields a value of $6.5 \pm 0.5\mu_B$ for the ordered Ho moment at 1.5 K. The error bar takes into account the uncertainty on the spin orientation, and a possible small remaining Mn moment ($<1\ \mu$B). The Ho moment almost reaches the value found in $HoMn_2$ [7.8(1) μ_B from Ref. 8; 7.1(1) μ_B from our data]. It remains well below the moment in $HoAl_2$ (9.18 μ_B),[22] which is close to the free ion moment (10 μ_B).

The temperature variation of the peak intensities (Fig. 3) allows one to determine the transition temperatures of the different phases. The incommensurate phase observed at ambient pressure has the highest transition temperature of 120 K. It is no longer observed under applied pressure. The SRO phase has a smeared transition around 40–60 K. The LRO pressure induced phases (canted and ferromagnetic) have the lowest transition temperature of 30 K, which appears to be independent of pressure.

In Fig. 4, we show the magnetic phase diagram deduced from our measurements. We interpret it as follows. The incommensurate phase has a very high transition temperature $T_N = 120$ K, close to the value found in YMn_2. So it is clearly associated with localized intrinsic Mn moments. It is

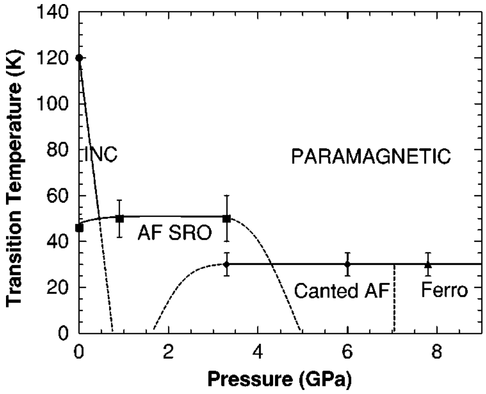

FIG. 4. Magnetic phase diagram of Ho($Mn_{0.9}Al_{0.1}$)$_2$ *versus* pressure. Regions below intersecting lines correspond to coexisting phases. Magnetic phases contributing to less than 15% of the intensity are discarded.

stable only in a narrow range of lattice constant[19] and results from dominant Mn-Mn exchange interactions, easily suppressed by a small pressure.

The most interesting result is the very unusual transition from the short range to long range order observed versus pressure. It is the first time that such transition is observed in RMn$_2$ compounds without changing the chemical content. The most obvious explanation is that it corresponds to a transition from intrinsic to induced Mn moments. Note that Al dilution, which increases the the transition temperature of the SRO phase,[23] is expected to stabilize intrinsic Mn moments. The spin disorder observed below the transition would naturally come from the presence of Mn-Mn interactions, competing with each other and with R-Mn and R-R ones. The onset of long range order at the transition reveals a change in the energy balance of the spin interactions, due to a weakening of the energy of Mn-Mn interactions.

The absence of a volume anomaly neither versus pressure nor versus temperature is surprising. A volume anomaly is expected when localized moments become itinerant, as observed for instance in YMn$_2$ at T_N. In the present case, it could mean that the volume anomaly is smeared by magnetic disorder. One could also think that intrinsic Mn moments remain localized in the paramagnetic regime, in contrast with YMn$_2$. Whatever the reason, we note that the magnetostructural anomalies observed in YMn$_2$ at T_N are strongly decreased by Al doping, and disappear below 10% substitution.[24,25]

The evolution of the LRO as pressure increases further is more straightforward. The LRO phase observed at intermediate pressures is similar to the canted phase of HoMn$_2$ and DyMn$_2$,[8] leading us to assume that only 1/4 of the Mn sites are magnetic and induced by Ho ones. Here, Mn-Mn nearest neighbor interactions cancel, and the stability of the canted structure is controlled by the balance between antiferromagnetic R-Mn and ferromagnetic R-R interactions. In DyMn$_2$, the ratio $J_{R\mathrm{Mn}}/J_{RR}$ between these interactions could be estimated to - 3.8.[23] It should be of the same order here. As pressure increases, induced Mn moments continue to decrease, as the Mn-Mn distance falls well below the instability threshold. Consequently, the contribution of R-Mn interactions to the total energy decreases. In a simple calculation with isotropic first neighbor exchange interactions only, the energy of the canted phase writes as

$$E=-J_{RR}S_R^2(3+\cos 2\psi)+6J_{R\mathrm{Mn}}S_R S_{\mathrm{Mn}}\sin\psi,$$

where ψ is the canting angle between the rare earth spin S_R and its ferromagnetic component, and S_{Mn} is the induced Mn spin. Minimizing the energy allows one to determine the variation of the canting angle, expressed as $\sin\psi = -3/2(S_{\mathrm{Mn}}/S_R)(J_{R\mathrm{Mn}}/J_{RR}) = -3g/4(M_{\mathrm{Mn}}/M_R)\ (J_{R\mathrm{Mn}}/J_{RR})$. Clearly, as the Mn moment decreases with increasing pressure, the canting angle decreases. At the highest pressures studied ($P \geqslant 7.8$ GPa), all Mn sites should be non magnetic, as in hexagonal Laves phases with short Mn-Mn distances. R-R interactions persist alone, stabilizing the ferromagnetic phase. These interactions are not frustrated but rather weak, as expected between $4f$ moments, thus the transition temperature is low. The Curie temperature ($T_C = 30$ K) compares very well with that in HoAl$_2$, a ferromagnet with $T_C = 27$ K.[22] Note that as soon as Mn moments vanish, we are left with stable R moments coupled by RKKY interactions. These interactions are not expected to be strongly affected by pressure, since they oscillate *versus* interatomic distance with a wavelength well above the typical variation induced by pressure. Therefore the transition temperature is pressure independent.

Our results show that at low Al content the main effect of Al substitution is that of a chemical negative pressure which tends to localize the spins on the frustrated Mn lattice and could be reversed by an applied pressure. The nature of Mn magnetism in the SRO phase could be clarified by studying spin fluctuations, in comparison with recent results in spin liquids and spin glasses.[27] The strong effect of Al doping is reminiscent of that observed in YMn$_2$ (Ref. 28) and beta-Mn,[29] also showing topological frustration and magnetic instability.

A very original effect of pressure is the onset of a long range ordered phase, arising from a disordered phase where pressure suppresses frustrated moments. Long range order results from a change in the energy balance of the spin interactions, from dominant Mn-Mn exchange to competing R-Mn and R-R ones, and finally to R-R exchange only. These changes are associated with changes in the nature of the Mn magnetism, from a localized to an induced then to a nonmagnetic state.

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