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Magnetic-field-induced transition in $BaVS_3$

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The metal-insulator transition (MIT) of $BaVS_3$ is suppressed under pressure, and above the critical pressure of $p_{cr} \approx 2$ GPa the metallic phase is stabilized. We present the results of detailed magnetoresistivity measurements carried out at pressures near the critical value in magnetic fields up to $B=12$ T. We found that slightly below the critical pressure the structural tetramerization—which drives the MIT—is combined with the onset of magnetic correlations. If the zero-field transition temperature is suppressed to a sufficiently low value ($T_{MI} \leq 15$ K), the system can be driven into the metallic state by application of magnetic field. The main effect is not the reduction of T_{MI} with increasing B, but rather the broadening of the transition due to the applied magnetic field. We tentatively ascribe this phenomenon to the influence on the magnetic structure coupled to the bond order of the tetramers.

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The nature of the metal-insulator transition (MIT) of $BaVS_3$ has presented riddles ever since its discovery a quarter of a century ago.[1,2] The ambient pressure MIT is spectacular in the susceptibility cusp,[1–4] but it is also manifested in specific heat,[5] thermal expansion,[3] resistivity,[1–4] and optical reflectivity[6,7] anomalies. The measurement of transport properties under pressure[2,3,8,9] revealed that the insulating phase is bounded by a line of MIT's in the p-T plane. The transition temperature T_{MI} drops to zero at the critical pressure $p_{cr} \approx 2$ GPa, and the high-pressure $p > p_{cr}$ phase is metallic down to the lowest accessible temperatures.[8]

The order of the MI phase transition was debated, and the options of a weakly first-order, second-order, and supercritical transition have all been put forward. However, resistivity[8] and in particular magnetoresistivity[9] measurements under pressure led us to favor a second-order transition. The character of the transition remains unchanged under pressures up to 1.5 GPa as it always corresponds to a sharp spike in the logarithmic derivative of the resistivity, $d \log \rho / d(1/T)$. This suggests a line of second-order MIT's. One purpose of the present study is to find out whether the same phase boundary is preserved above 1.5 GPa extending up to the critical pressure.

A critical line is possible only if it separates phases of different symmetry, so the MIT in $BaVS_3$ must be at the same time an ordering transition breaking some global symmetry.[10] However, the ambient-pressure MIT at 69 K is not accompanied by the appearance of detectable magnetic moments, and the first two decades of search failed to reveal a symmetry-changing distortion at T_{MI}.[11] Finally, in 2002 Inami *et al.* reported a doubling of the unit cell along the trigonal c axis.[12] Since the unit cell of the $T > T_{MI}$ structure contains two V atoms along the c axis,[13] the $T < T_{MI}$ unit cell must contain four; hence, the symmetry breaking change corresponds to tetramerization. More recent x-ray scattering measurements reconfirmed the existence of four inequivalent V sites at low temperatures.[14–16] The x-ray measurements were extended to 5 K, well below the third and lowest transition temperature $T_X=30$ K of $BaVS_3$. The mysterious T_X transition leads to a low-T phase with incommensurate magnetic long-range order,[17] and possibly orbital order,[18] but the symmetry of the lattice is held at T_X.[14–16]

The pressure range 1.5 GPa $< p < p_{cr}$, where $T_{MI}(p)$ drops below ≈ 20 K, had not been studied in detail. It is expected that novel behavior may arise if the structural transition and the magnetic transition eventually meet, or even only get near. As T_X was found to be pressure independent in the pressure range investigated ($p < 1$ GPa),[19] the $T_{MI}(p)$ and $T_X(p)$ lines may merge, which could change the nature of the MIT.

Another consideration is that even the well-studied low-pressure MIT has a dual nature: it is the boundary of a phase with spontaneous symmetry breaking (tetramerization) and, at the same time, a metal-insulator phase boundary. Since the MIT coincides with a symmetry breaking transition, the phase boundary may in principle be continued to a zero-temperature quantum critical point. On the other hand, general arguments suggest that a metal-insulator transition is likely to become first order before the predicted gap could become too small.[20] Furthermore, it has been pointed out that the quantum critical behavior of an MIT may be quite unlike the quantum criticality of a mere symmetry breaking transition.[21] $BaVS_3$ has both aspects; thus, it presents a situation of general interest but little firm knowledge.

In this paper we investigate if there is a change in the nature of the MIT at pressures close to the critical value. In order to get detailed information about the range where $T_{MI}(p)$ is suppressed to zero, we carried out magnetoresistance measurements at pressures where the characteristic energy of the applied field is comparable to that of the transition temperature. Results related to the MIT are presented here, while studies about the high-pressure metallic phase will be reported in a companion paper.[22]

Single crystals of $BaVS_3$ were grown by the tellurium flux method. The crystals, obtained from the flux by sublimation, have typical dimensions of $3 \times 0.5 \times 0.5$ mm^3. The space group of the crystals ($P6_3/m2/m2/c$) and the lattice parameters ($a=6.721, c=5.623$) were identified by a Philips PW

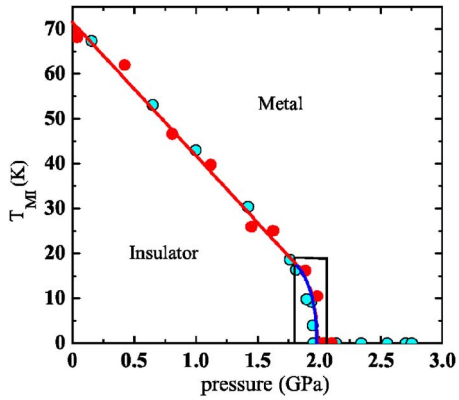

FIG. 1. (Color online) Pressure dependence of the metal-insulator phase boundary, as identified by the peak in the logarithmic derivative of the resistivity. Results for two samples, marked by different symbols, are presented. The boxed range indicates the interval where results presented in the following figures were obtained.

1100 single-crystal diffractometer. The sample used in the present study was inserted into a self-clamping cell with kerosene as a pressure medium. The pressure was monitored *in situ* by an InSb sensor. The hydrostatic pressure was stable within 0.05 kbar in the pressure and temperature ranges investigated in this work. The resistivity of the single crystal was measured in a standard four-probe arrangement. The current was kept low enough to avoid the self-heating of the sample. Magnetic fields up to 12 T were applied perpendicular to the current, flowing along the crystallographic c direction.

The zero-field pressure dependence of the metal-insulator phase boundary is shown in Fig. 1. The boundary consists of two distinguishable parts: T_{MI} decreases with p almost perfectly linearly to about $p \approx 1.8$ GPa where the insulator becomes much softer, and the boundary begins to drop steeply towards zero, signifying a new regime of the MIT. The almost vertical drop of the $T_{\mathrm{MI}}(p)$ curve makes it difficult to map this region in detail. The points in the boxed range of Fig. 1 represent the data obtained by attempting to fine-tune the pressure up to p_{cr}. Even at $p=1.98$ GPa where T_{MI} is as low as to 7.5 K, the usual characterization of the transition by $d \log \rho / d(1/T)$ or magnetoresistivity curves yielded no striking difference from the behavior seen up to 1.5 GPa.[9] By these criteria, the transition at 1.98 GPa is still second order. However, the considerable smearing out of the phase transition by magnetic field—in addition to the downturn of the phase boundary—indicates that the character of the MIT changes in the parameter range $p > 1.8$ GPa, $T \leq 20$ K (this domain is not sharply delineated).

Former magnetotransport studies up to 1.5 GPa showed that the low-field phase boundary follows a quadratic shape[9]—i.e., $\Delta T_{\mathrm{MI}}(p,B)/T_{\mathrm{MI}}(p) \propto [B/B_c(p)]^2$, where the pressure-dependent critical field and the zero-field transition temperature scale together according to $\mu_B B_c(p) = 1.7 k_B T_{\mathrm{MI}}(p)$. In the case of the $p=1.5$ GPa measurement—and for any lower pressures—no broadening of the transition was observed up to the highest field investigated, $B_{\max} = 12T$. Taking $T_{\mathrm{MI}}(p)$ as the characteristic energy scale,

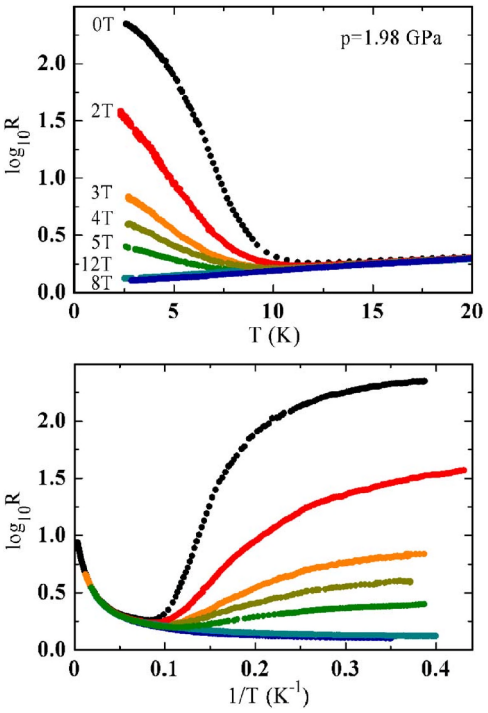

FIG. 2. (Color online) Temperature dependence of the resistance measured in presence of various magnetic fields at $p=1.98$ GPa. At this pressure with increasing magnetic fields $BaVS_3$ undergoes a field-driven insulator-to-metal transition.

this field corresponds to $B_{\max} \approx \frac{1}{5} T_{\mathrm{MI}}$. In contrast, in the high-pressure range $p > 1.8$ GPa the transition is considerably smeared out by magnetic fields smaller than $\frac{1}{5} T_{\mathrm{MI}}$, as shown in Fig. 2. This implies that in the new regime of the transition—i.e., in the boxed range of Fig. 1—the insulating phase became considerable less stable against the change of pressure and the application of magnetic field. We guess that the arising of an electronically soft state of matter is due to the presence of competing orders.

We also found that if T_{MI} is suppressed below ≈ 15 K, then the metallic state can be reached by applying magnetic field. Such a field-driven metal-insulator transition is shown in Fig. 2 for $p=1.98$ GPa, where at zero magnetic field the transition temperature is $T_{\mathrm{MI}}=7.5$ K. At low fields the low-temperature resistivity is monotonically increasing with decreasing temperature, indicating an insulating state. However, at high fields the temperature dependence changes character and the ground state of the system is metallic. At the lowest temperature of the experiments ($T=2.5$ K) there is a more than two-orders-of-magnitude change in the resistance. This huge magnetoresistance is clearly due to the suppression of the charge gap. The field-induced insulator-to-metal transition has taken place well below $B_c(p)$ derived from the low-pressure scaling rule, which would be $B_c = 18$ T at this pressure. This also implies that the transition in the boxed regime of Fig. 1 has a different character, and we investigate this point in more detail below.

Figure 3 presents an example for the magnetic field dependence of the resistance at various temperatures for $p=1.8$ GPa. At this pressure—in absence of a magnetic

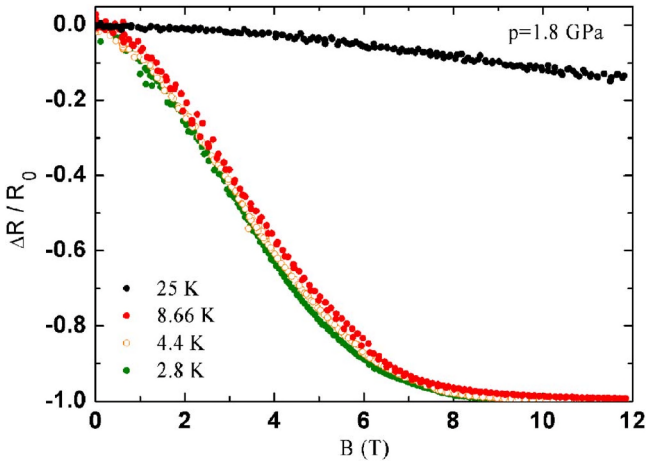

FIG. 3. (Color online) Magnetic field dependence of the resistance measured at various temperatures at $p=1.8$ GPa. (The data are normalized to the zero field values.) The low-temperature curves are examples of the field-driven insulator-to-metal transition. For comparison the magnetoresistance measured at $T=25$ K is also shown.

field—the system is insulating below the transition temperature of $T_{MI}=13$ K. The B sweeps reveal that the metallic state is restored by the application of a magnetic field. The drop of the resistance is smooth; no sharp transition can be identified at any temperatures. When the data are normalized to the zero-field values, the variations seem rather similar to each other at all temperatures. We should, however, emphasize that the change of the resistance is huge—at $T=2.8$ K it is more than three orders of magnitude—thus it should again be attributed to the suppression of the charge gap.

The overall character of the field-induced transition is best revealed by the three-dimensional plot of $\log R$ over the B-T plane. This is shown for $p=1.8$ GPa in the upper panel of Fig. 4. Here the $R(B,T)$ surface is constructed from the experimental B and T sweeps; beside the results shown in Fig. 3, this plot includes also T sweeps at various magnetic fields. It is clear that at $B=0$ the system is most insulating at low T, while the drive towards the conducting state looks quite similar in B and T directions.

The transition temperature is generally identified with the position of the peak in the logarithmic derivative of the resistivity. The middle and bottom panels of Fig. 4 show the $d\log R/d(1/T)$ curves over the B-T plane. The top view of the color-coded surface illustrates the magnetic field dependence of the transition temperature. Though this might imply that a certain point $T_{MI}(B)$ drops sharply as a function of the magnetic field and a field-induced first-order transition takes place,[23] the side view of the surface reveals that the main effect of the magnetic field is not the shifting of the cusp in the derivative, but rather its general suppression.

The same analysis of the data recorded at $p=1.98$ GPa (Fig. 5) shows that with increasing pressure the insulating domain shrinks and the transition temperature is shifted down, but the general features remain unchanged. Again, by increasing B, the transition becomes ill defined, indicating that the character of the high-pressure MIT is definitely different from that of the low-pressure (say, $p<1.5$ GPa) sharp

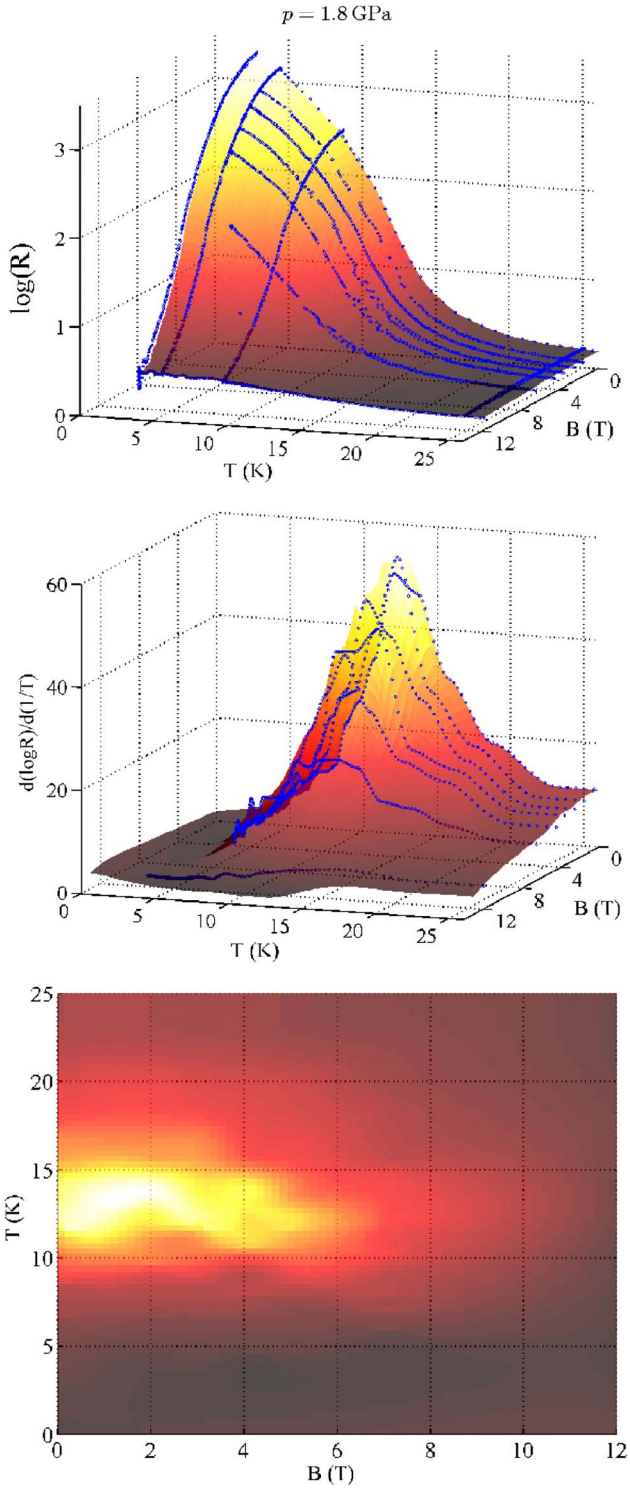

FIG. 4. (Color online) Three-dimensional plots obtained by temperature and magnetic field sweeps at $p=1.8$ GPa (from light to dark: from highest to lowest values). Upper panel: $\log\rho$ over the B-T plane. The field gradually suppresses the insulating character. Middle panel: plotting $d\log\rho/\mathrm{d}(1/T)$ over the B-T plane shows that the field-induced transition gets weaker and less easily defined at higher fields. Lower panel: top view of the middle panel—i.e., the magnetic field dependence of the transition temperature derived from the cusplike anomaly in the temperature dependence of $d\log\rho/\mathrm{d}(1/T)$.

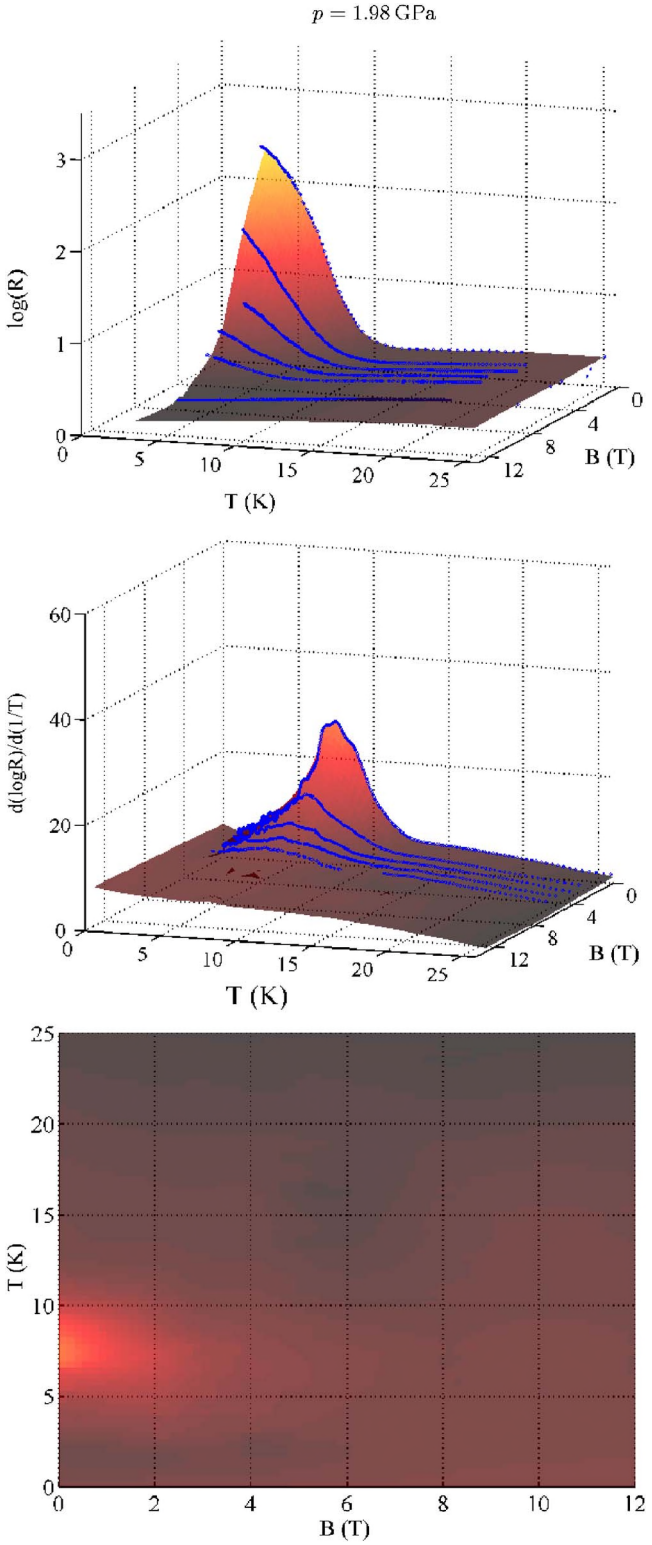

FIG. 5. (Color online) Three-dimensional plots obtained by temperature and magnetic field sweeps at $p=1.98$ GPa. Upper panel: $\log \rho$ over the B-T plane. Lower panels: $d \log \rho / d(1/T)$ over the B-T plane (from light to dark: from highest to lowest values). A comparison to Fig. 4 reveals that with increasing pressure the insulating domain shrinks.

transition. We interpret the observed broadening as a sign that magnetic ordering phenomena (related to those appearing at the low-pressure ordering transition at T_X) begin to interfere with the MIT, from $p \sim 1.8$ GPa upwards or $T_{\mathrm{MI}} \sim 20$ K downwards.

The suppression of nonferromagnetic order by magnetic field is a common phenomenon but it is not necessarily associated with the broadening of the transition. There are many systems (including ordinary antiferromagnets) which possess breakable symmetries even in the presence of an external magnetic field. This residual symmetry can be broken by an order parameter which is not induced by the field. The critical temperature decreases with increasing B but the transition remains well defined. An example is given by the spin-density-wave system of $(TMTSF)_2PF_6$ which continues to undergo a sharp phase transition around $T=10$ K even in magnetic fields as high as $B \approx 30$ T.[24]

$BaVS_3$ is definitely not in the above category; the metal-insulator transition is considerably broadened in fields as demonstrated in Figs. 4 and 5. There are two possibilities: either the order of the phase is induced by the field (thus in the presence of the external field there is no symmetry breaking and the transition becomes ill defined) or the observed phenomena are kinetic and cannot be explained in the language of equilibrium phase transitions.

Taking the first possibility, the field induces in linear order the corresponding components of spin and orbital momentum. This is relevant if the low-T phase $BaVS_3$ possesses a net ferromagnetic moment (since the ferromagnetic moment may be very weak, it may have escaped experimental detection). Even if the zero-field ground state carries no total magnetization, the field could also induce higher-order uniform moments. If one of these is mixed into the order parameter of $BaVS_3$ at $T<T_X$, the observed broadening may once again follow.

Future experiments will decide whether the broadening of the transition can be explained in terms of equilibrium phases, as described above. However, we wish to point it out that there is an alternative: namely, that the broadening is a relaxation effect and thus not explicable within the framework of equilibrium phase transitions in ideal systems.

There is an independent observation showing that the character of the MIT changes, and becomes mixed with, or preceeded by, magnetic ordering phenomena in this p-T regime; above $p \sim 1.8$ GPa hysteresis loops may appear both in B cycles and in T cycles.[2,22] The shape of the hysteresis loops depends on the sweep rate, suggesting that we are dealing with a relaxation phenomenon. Hysteresis appears both above and below the critical pressure; thus, it is plausible to relate it to the complicated long-period order which was observed by magnetic neutron scattering.[17–19] Similar, so-called weak relaxation effects were observed in incommensurate density-wave systems and successfully interpreted in the picture of a nonideal system going through a hierarchy of pinned states.[25] Formally, the random impurity pinning leads to a broad distribution of the relaxation times, and this results in logarithmic, power law, or stretched exponential relaxation. The finding that the ambient-pressure low-T phase of $BaVS_3$ displays a magnetic order which is incommensurate both in the basal plane and along the c axis[19] may provide

the key elements for an analogous relaxation mechanism. If an incommensurate structure is locally pinned to defects, while the optimal wave number is temperature dependent, the temperature sweep yields an inhomogeneous state which tries to relax towards the optimal structure with a locally varying rate.

To summarize, we investigated the high-pressure low-temperature region where the insulating phases are suppressed. The zero-field boundary was followed down to $T_{\mathrm{MI}} \approx 8$ K. We did not directly see a first-order jump in either the temperature, or the pressure, or the field dependence, but in the range $T_{\mathrm{MI}} < 20$ K, $p > 1.8$ GPa we observed a considerable smearing out of the phase transition by magnetic field. We suggest that this is a sign that the metal-insulator transition $T_{\mathrm{MI}}(p)$ and magnetic ordering phenomena $T_X(p)$ appear combined in this pressure regime.

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