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Verwey transition in Fe_3O_4 at high pressure: Quantum critical point at the onset of metallization

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We provide evidence for the existence of a *quantum critical point* at the metallization of magnetite Fe_3O_4 at pressure $p_c \approx 8$ GPa. We show that the present ac magnetic-susceptibility data support earlier resistivity data. The Verwey temperature scales with pressure $T_V \sim (1-p/p_c)^\nu$ with $\nu \sim 1/3$. The resistivity data show a temperature dependence $\rho(T)=\rho_0+AT^n$ with $n \simeq 3$ above and 2.5 at the critical pressure, respectively. This difference in n with pressure is a sign of critical behavior at p_c. The magnetic susceptibility is smooth near p_c, both at the Verwey transition and near the lower temperature ferroelectric anomaly.

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Magnetite (Fe_3O_4) is among the oldest and most fascinating materials throughout the history of science. It is ferrimagnetic below the Curie temperature $T_C \approx 860$ K and semiconducting with a room-temperature resistivity of $\rho(T=300\text{ K}) \simeq 10^{-2}$ Ω cm. The (almost) stoichiometric material undergoes a discontinuous Verwey transition[1] to a higher-resistivity phase at a temperature $T_V \simeq (121 \pm 1)$ K, at which the resistivity at ambient pressure jumps up by about two orders of magnitude. The transition is of a semiconductor-semiconductor type at lower pressures, although the exact difference between them remains somewhat elusive. In addition, the net magnetic moment has the value $\mu \simeq 4.1\mu_B$ per formula and approximately corresponds to the spin $S=2$ in Fe^{2+} high-spin configuration in the octahedral position (the remaining two Fe^{3+} ions, one in tetrahedral and one in the octahedral positions with spin $S=5/2$ have their moments antialigned). The high-spin state is induced by Hund's rule coupling (strong correlations) among $3d$ electrons.

Essential progress was made when samples with an extremely well-controlled composition were synthesized[2] and studied.[3] Notably, the change of the Verwey transition from first to second order has been discovered, depending on the off-stoichiometry parameter δ of $Fe_{3-\delta}O_4$. Also, the metallization of Fe_3O_4 has been achieved[4] at a pressure of $p_c \simeq 8$ GPa.

The primary purpose of this work is to systematize the change in the properties of Fe_3O_4 with pressure and to single out universal features of the results. During the course of this work, we reanalyzed the earlier resistivity data[4] and have discovered that the combined magnetic-susceptibility and resistivity data point to the possibility of a *quantum critical point* existing at the metallization threshold, at which a specific scaling is observed. This is explicitly verified by determining the pressure dependence of the critical exponents of both the transition temperature $T_V(p)$ and the resistivity just above the transition $\rho(T_{V+})$, as well as that of $\rho(T)$ at the critical pressure and above it. Also, the pressure dependence of the two low-temperature anomalies in the ac susceptibility—presumably connected with the appearance of ferroelectricity—evolves with increasing pressure, but this will not be detailed here. We also point out that an additional transition or crossover line between metallic (M) and semiconducting (SC) phases should occur.

The importance of the presence of a quantum critical point (QCP) at the localization-delocalization boundary cannot be underestimated as there are no well-defined *universality classes* yet for the electronic transitions. Previously, a *classical* critical point (of the Van der Waals type) was determined[5] in a three-dimensional system of Cr-doped V_2O_3 at $T_{\text{crit}}=457.5$ K and at $p_{\text{crit}} \simeq 3.7$ kbar, the existence of which was suggested earlier.[6] Recently, a critical point has been seen[7] in a quasi-two-dimensional organic solid at $T_{\text{crit}}=39.7$ K and $p_c=24.8$ MPa, with completely different critical exponents than those for the above three-dimensional case. A true QCP (at $T=0$) at the localization-delocalization boundary has been detected at the Kondo semiconductor—non-Fermi-liquid boundary upon chemical substitution in $CeRhSb_{1-x}Sn_x$.[8] In the last system, it is connected with the delocalization of $4f$ electrons due to Ce^{3+} and is induced by the change in carrier concentration upon doping. We suggest that the present system (Fe_3O_4) represents a different example of a system with a true QCP (with $T_{\text{crit}}=0$) in a monocrystalline and almost stoichiometric system in a spin-polarized state. In contrast, a different type of behavior was observed[9,10] in the antiferromagnetic system $NiS_{2-x}Se_x$, in which the Hund's rule coupling, which is leading to the high-spin ($S=1$) state, also occurs. The differences are caused by a disparate magnetic ordering, as well as by the circumstance that—as we show—the metallic state of Fe_3O_4 is that of a *non-Fermi liquid*, whereas metallic state of $NiS_{2-x}Se_x$ is that of an almost localized Fermi liquid.

Single-crystal sample used for ac magnetic-susceptibility measurements was cut from a larger crystal grown from the melt using the cold crucible technique. The crystal was then annealed under CO/CO_2 gas mixtures to establish the stoichiometry[2] and rapidly quenched to room temperature to freeze in the high-temperature thermodynamic equilibrium. Although this procedure generates octahedral defects, most of the low-temperature electronic processes remain intact, as is evidenced by the sharp Verwey transition temperature T_V

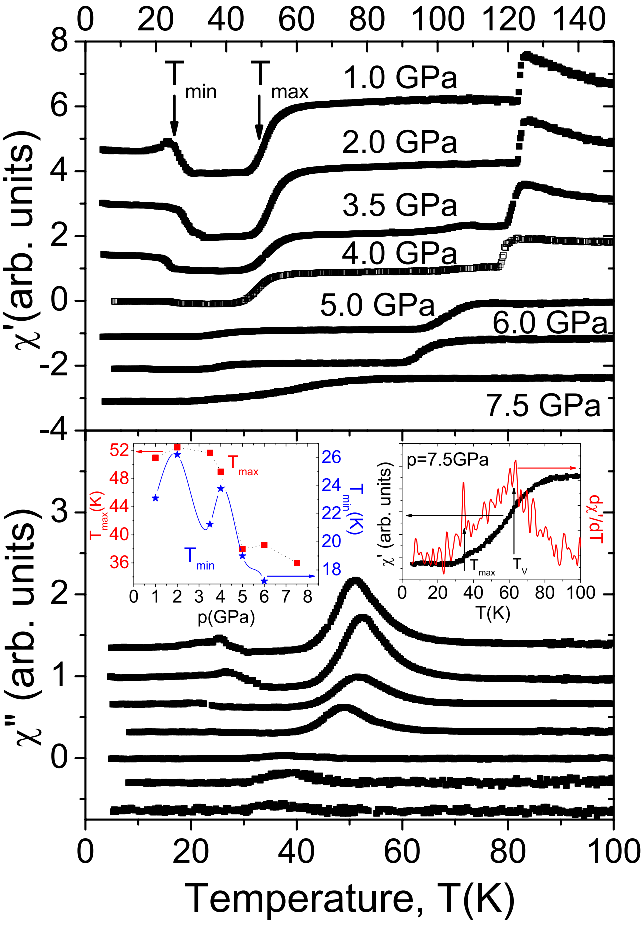

FIG. 1. (Color online) Pressure dependence of ac magnetic susceptibility (at a frequency of 120 Hz) for the stoichiometric single crystal; note different T scales for the real (χ') and the imaginary (χ'') parts of χ. Right inset: illustration of the definition of T_V from maximum of $d\chi'/dT$ when the sharp step in χ' was not observed (i.e., for $p>3.5$ GPa). Left inset: $T_{\max}$ indicates the position of the anomaly near 50 K, whereas $T_{\min}$ is the lower anomaly (indicated by the vertical arrows).

and the existence of the low-temperature anomaly (observed only in the best crystals). The pressure experiments on single crystal were carried out in a cylinder with 0.7 and 1.5 mm as radius and length, respectively. The sample and the coil system were inserted with fluorinert into teflon holder and compressed with six WC anvils. The hydrostatic condition quality was very good.

In Fig. 1 we display the temperature dependence of the ac susceptibility $\chi=\chi'+i\chi''$ components for selected pressures. The upper panel provides the real part χ', for which three characteristic temperatures are: the Verwey temperature T_V (the uppermost jump) and the *two temperatures associated with ferroelectricity*[11] for $T_{\max}\sim 60-50$ K, and the lower anomaly at $T_{\min}\sim 20$ K. With increasing pressure, all of them shift toward lower temperatures and eventually disappear for pressures $p\gtrsim 7.5$ GPa. Note that pronounced losses are observed near $T_{\max}$. They are most probably due to the ferroelectric transition and associated with it ferroelectric domain dynamics. In the insets, we mark the temperatures T_V, $T_{\max}$, and $T_{\min}$ near the critical pressure. The first two temperatures approach each other as well as decrease with increasing pressure.

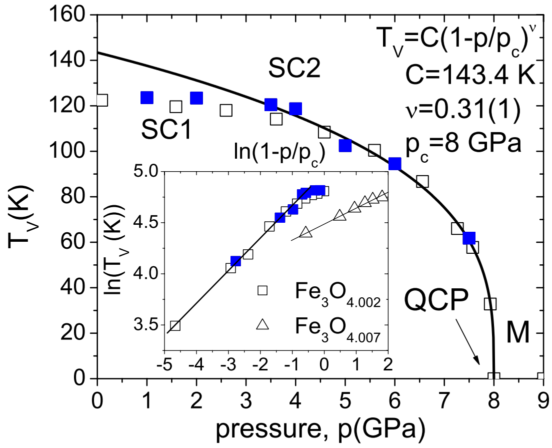

FIG. 2. (Color online) Pressure dependence of the Verwey transition temperature T_V. We mark the data points from this work as solid squares (blue online) and those of Môri *et al.* (Ref. 4) by open squares. Solid line represents the fit specified above and ending at quantum critical point (QCP). Inset: same in the doubly logarithmic scale. Open triangles show the respective critical behavior for slightly nonstochiometric ($\delta=0.007$) sample. M denotes a stable metallic state, whereas SC labels the semiconducting states both below and above T_V for $p\lesssim 7.5$ GPa.

To demonstrate the evolution of the Verwey transition with pressure, we plot in Fig. 2 the $T_V(p)$ dependence by combining our magnetic-susceptibility results and the resistivity data taken from Ref. 4. In the inset, we redraw the data on a doubly logarithmic scale for both of the almost stoichiometric ($Fe_3O_{4.002}$) and the nonstoichiometric ($Fe_3O_{4.007}$) samples to demonstrate the power-law fit quality, as well as to show the difference between the two cases. We observe a clear behavior of $T_V(p)=C(1-p/p_c)^{\nu}$ above 3.5 GPa for the almost stoichiometric sample with the critical pressure $p_c\simeq 8$ GPa and the value of the exponent $\nu\simeq 1/3$. As the data in the inset show, both p_c and ν depend strongly on the sample stoichiometry. For example, for $\delta=0.007$ we have $p_c\simeq 6.1$ GPa and the critical exponent is reduced to the value $\nu\simeq 1/6$. This means that the nonstoichiometry *is not* equivalent to a reduction in critical pressure.

One can draw a very important conclusion from Fig. 2. As the Verwey transition for $p\lesssim 7.5$ GPa is of semiconductor-semiconductor type and for $p>8$ GPa the ground state is metallic, there must exist an additional transition or crossover line starting from $p=p_c$, which separates M and SC states. In effect, a V shape curve should be expected to originate from $p=p_c$, a behavior detected near QCP in other correlated systems.[7] The regime within the V curve constitutes the *quantum critical regime*.

The nature of the metallic state (M) above p_c should be characterized in greater detail. This is particularly important because, for $p<7.5$ GPa, the state *above* T_V is clearly a semiconductor. A (qualitatively) similar type of behavior to that exhibited in Fig. 2, though without any reference to *quantum critical behavior*, was suggested by Rozenberg *et al.*[12] Also, the magnetic-susceptibility and the resistivity[4] discontinuities in Fig. 2 follow the same dependence $T_V(p)$.

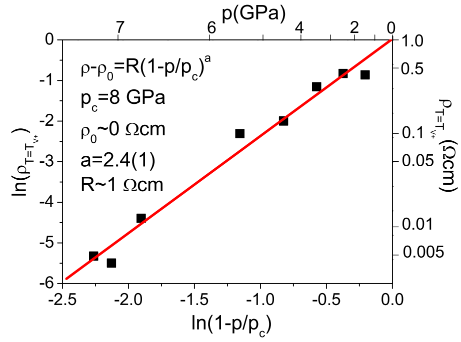

FIG. 3. (Color online) Pressure dependence of the electrical resistivity just above the Verwey transition (Ref. 4) (at $T=T_{V+}$). The residual resistivity obtained from the fit is $\rho_0 \simeq 0$ within the fitting error.

To provide quantitative evidence that we observe a criticality near the $T_{\text{crit}}=0$ and $p=p_c$ point, one requires a proper definition of the order parameter as well as its dependence on $p-p_c$. In the previous studies of criticality near the insulator-metal transition,[5,7] the role of the order parameter was played by the conductivity difference $\sigma(p)-\sigma(p_c)$ or, equivalently, directly by the resistivity.[9] The two transport quantities mimic the essential difference between carrier concentrations on both sides of the electronic transition in the equilibrium state. Additional evidence is provided by the behavior of physical quantities near p_c. For that purpose, our data from Fig. 1 is not directly useful, as the susceptibility is continuous upon approaching the system metallization. This in turn means that magnetism is robust under the applied pressure, as no clear signature of *critical magnetic behavior* has been observed up to 300 K. In view of that circumstance, we reanalyzed the data of Môri *et al.*[4] and plot in Figs. 3 and 4, respectively, the resistivity $\rho(T_{V+})$ just above the Verwey transition as a function of $p-p_c$ as well as $\rho(T)$ at Fe_3O_4. We observe that, in the former situation, we have (roughly) the scaling $\rho(p)=R[(p_c-p)/p_c]^a$ with $R \simeq 1$ Ω cm and $a \simeq 5/2$, whereas at $p=p_c$: $\rho(T)=\rho_0+AT^n$ where $\rho_0 \simeq 35.5$ $\mu\Omega$ cm and $n \simeq 5/2$. These results differ from those for Mott-Hubbard systems[5,7,9] obtained when the critical temperature $T_{\text{crit}}>0$. However, it should be underlined again that, as only in the present case $T_{\text{crit}}=0$, we are dealing with a true quantum critical regime for $p \to p_c$.

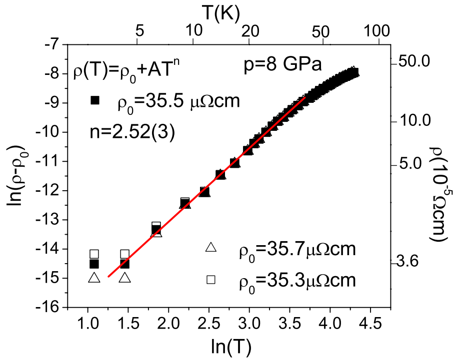

FIG. 4. (Color online) Temperature dependence of electrical resistivity $\rho(T)=\rho_0+AT^n$ of $Fe_3O_{4.002}$ at $p_c=8$ GPa. The solid line (red online) corresponds to $\rho_0=35.5$ $\mu\Omega$ cm and $n=2.52$. Open symbols show the sensitivity of the fits to ρ_0 value: slight variations of the ρ_0 value do not appreciably change the fitting accuracy.

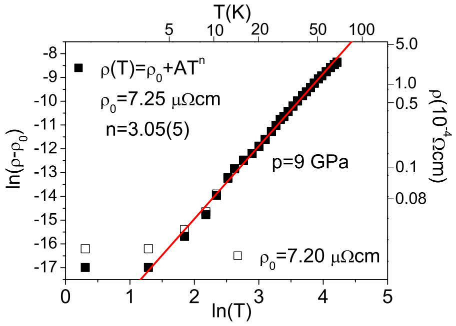

FIG. 5. (Color online) Temperature dependence of resistivity $\rho(T)=\rho_0+AT^n$ in the metallic (M) regime for $Fe_3O_{4.002}$. The solid line corresponds to $\rho_0=7.25$ $\mu\Omega$ cm and $n=3.05$. The fitting accuracy does not change under a minute change of ρ_0 as shown.

In Fig. 5 we plot the temperature dependence of the resistivity in the metallic phase (for $p=9$ GPa). The resistivity $\rho(T)$ is roughly proportional to T^3 and the value of the residual resistivity is considerably reduced. The reduction in ρ_0 upon further metallization means that scattering on charged impurities (Fe^{2+} or Fe^{3+} vacancies) is reduced, since they are screened more effectively with increasing pressure. Note also the extreme sensitivity of the fitting upon the choice of the ρ_0 value. Parenthetically, this sensitivity may be regarded as an additional criterion of the sample quality.

The well-defined power-law behavior of both the pressure and temperature dependencies of the resistivity does not match those observed near the QCP for a ferromagnetic and antiferromagnetic systems[13] or those mentioned here for the antiferromagnetic systems near the critical point for the Mott-Hubbard transitions.[5,7,9] In other words, the metallization of Fe_3O_4 represents a separate universality class of phase transitions. In connection, it would be very interesting to compare them in detail with those[9] for the antiferromagnetic NiS_2, a Mott-Hubbard insulator at $p=T=0$, for which the Hund's rule also plays as important a role as for the ferrimagnetic state of Fe_3O_4.

On phenomenological grounds, one can relate the thermodynamics of the Verwey transition to the charge-order transition in the octahedral sites, which are connected with the freezing of the resonating electron between $Fe^{3+}-Fe^{2+}$ configurations of the two ions at T_V.[14] Considering the extra electron ($Fe^{2+}=Fe^{3+}+e^-$) as undergoing Mott-Wigner localization,[15] one can write down a phenomenological Ginzburg-Landau functional, albeit with a fermionic form of the configurational entropy for the spinless (i.e., strongly polarized) fermions, and rationalize a change over from the first to second order upon varying the system stoichiometry.[3]

In recent years the above picture was investigated using spectroscopic methods.[16] A pressure-induced transformation from the inverse to the normal spinel structure was claimed to occur.[12,17] Nevertheless, in spite of the complications of the situation in which both strong electronic correlations and electron-lattice coupling are important, a partial charge ordering was detected by x-ray scattering.[18] This last result means that strong correlations must play a primary role in the transition. This is because a relatively simple power-law behavior of $T_V(p)$, $\rho(T,p_c)$, and $\rho(T,p>p_c)$ means that the underlying mechanism of the transition should be physically simple. Otherwise, the change of T_V from above 120 K to zero should be sizably influenced by, e.g., the difference in thermal occupation of the low-energy phonons and, hence, lead to nonuniversal behavior.

In summary, we have demonstrated that the metallization of magnetite under pressure is described by a simple power-law scaling of physical properties including the transition temperature T_V, the resistivity near the critical pressure $\rho(p,T_{V+})$ at the transition, and, as a function of temperature $\rho(p=p_c,T)$, at p_c and above. These properties provide direct evidence of critical behavior with a QCP at $p_c \approx 8$ GPa. It is also suggested that the strong electronic correlations lead to a partial charge order (and concomitant with it partial localization) and may be the source of the observed volume change as it is the case for Mott-Hubbard systems.

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