Physica B 404 (2009) 2894–2897

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Verwey transition in magnetite at high pressure: A new quantum critical point at the onset of metallization

J. Spałek [a,b,*], A. Kozłowski [b], Z. Kąkol [b], Z. Tarnawski [b], Y. Fukami [c], F. Ono [c], R. Zach [d], L.J. Spalek [e], J.M. Honig [f]

[a] Marian Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland
[b] Department of Solid State Physics, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland
[c] Department of Physics, Okayama University, Okayama 700-8530, Japan
[d] Institute of Physics, University of Technology, Podchorążych 1, 30-084 Kraków, Poland
[e] Quantum Matter Group, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK
[f] Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA

ARTICLE INFO

PACS:
71.30.+h
71.27.+a
05.70.Jk

Keywords:
Verwey transition
Quantum critical point
Magnetite metallization
Semiconductor-metal transition

ABSTRACT

We provide a detailed physical discussion of the existence of a *quantum critical point* (QCP) at the metallization threshold of an almost stoichiometric magnetite, with the critical pressure $p_c = 8$ GPa. A presence of an additional crossover or a critical line separating metallic and semiconducting states is proposed. A connection of the critical behavior to that of a spinless-fermion model with coupling of fermions to the lattice distortion is outlined.

1. Introduction

The metallization of magnetite under pressure [1] in the range 7.5−8 GPa differs from the ordinary Mott–Hubbard transition by the presence of the high-spin state (Hund's-rule coupling) and the fluctuating valence between the essentially ionic states $Fe^{2+} \leftrightarrow Fe^{3+}$ in the octahedral positions. We have shown very recently [2] that when approaching the metallization, the electrical resistivity [1] and our *ac* susceptibility measurements scale the same way with increasing pressure and exhibit a well defined quantum critical point, at which the semiconductor–semiconductor Verwey transition disappears at temperature $T = 0$. However, the question still remains as to what happens to the Verwey semiconductor–semiconductor first-order transition line at $T > 0$ for the pressure $p \geq p_c$. This question is the main issue addressed here, as well as that concerning the critical exponent meaning at the Verwey temperature $T_V = T_V(p)$. The striking simplicity of the transition scaling behavior is elucidated.

* Corresponding author at: Marian Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland. Tel.: +48 12 6635685; fax: +48 12 6334079.
E-mail address: ufspalek@if.uj.edu.pl (J. Spałek).

0921-4526/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2009.07.079

2. Properties near quantum critical point

The 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 [3] 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 and the existence of the low-temperature anomaly (observed only in the best crystals). The single-crystal pressure experiments 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 a teflon holder and compressed with six WC anvils. The hydrostatic condition quality was very good.

In Fig. 1 we display magnetic *ac* susceptibility results discussed in detail in Ref. [2]. There is a well defined discontinuity at the uppermost (Verwey) transition temperature that fades away with increasing pressure. The low-temperature (ferroelectric) anomalies will not be discussed here [4], apart from specifying the characteristic temperatures in the lower-panel left inset. The qualitative characteristic consists of a quasicontinuous character of the Verwey transition, starting from $p \simeq 5$ GPa. Therefore, the

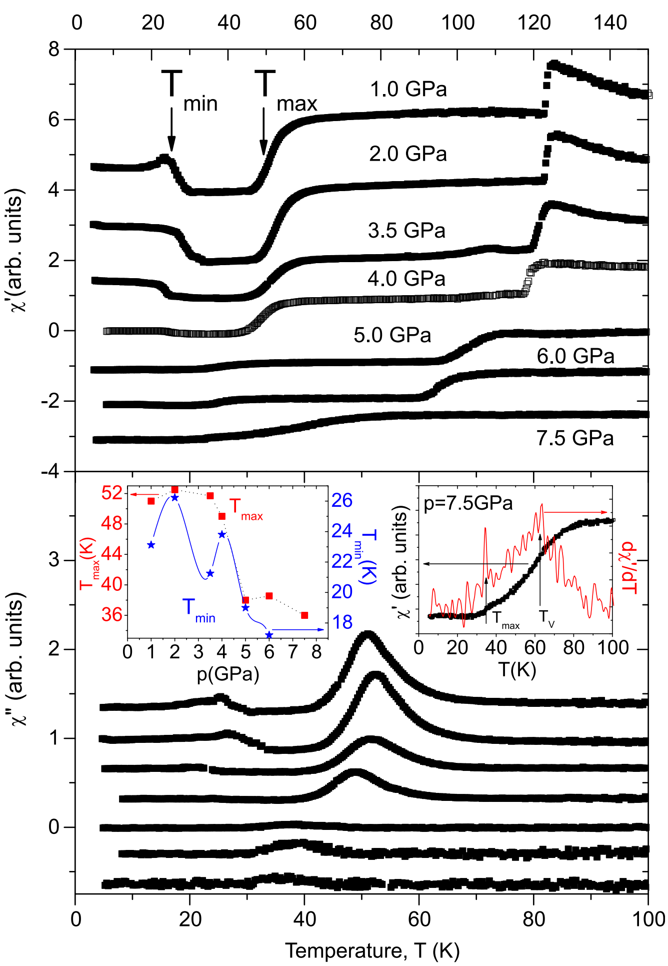

Fig. 1. (color online) Pressure dependence of ac magnetic susceptibility χ (at a frequency of 120 Hz) for the almost stoichiometric single crystal; note different T scales for the real (χ') and the imaginary (χ'') parts of χ. Right inset: illustration of the definition of T_V from maximum of $d\chi'/dT$ when the sharp step in χ' was not observed (i.e. for $p \geq 5$ GPa). Left inset: T_{max} indicates the position of the ferroelectric anomaly near 50 K, whereas T_{min} the lower anomaly (as indicated by the vertical arrows).

value of T_V has been determined by taking the derivative $d\chi'/dT$ of the real-part of the susceptibility, as illustrated in the right inset to the lower panel. Parenthetically, in that inset we show also that T_V is still well defined at $p = 7.5$ GPa; this fact justifies our taking of $p_c = 8$ GPa, not 7.5 GPa [1] (see also Fig. 2). The losses, as measured by the imaginary part of the susceptibility χ'' (cf. lower panel), are associated with the incipient ferroelectricity [5]. The conclusion from the upper panel is that there is a well defined magnetic signature of the Verwey transition concomitant with the electrical-transport discontinuities, as discussed next.

To illustrate explicitly the evolution of the Verwey temperature, we have drawn in Fig. 2 the pressure dependence of the Verwey temperature derived from both the electrical [1] and the above magnetic-susceptibility data. A well defined common exponential decrease of T_V with increasing p is observed, with the characteristics specified in the figure.

Note that in the inset we have drawn the $T_V(p)$ dependence for two samples $\delta = 0.002$ and 0.007, where the cation deficiency parameter is defined through the formula $Fe_3O_{4+\delta}$. The corresponding values of the critical exponent ν are $\approx \frac{1}{3}$ and $\frac{1}{6}$, respectively. Such large difference in the value of the critical exponent suggests the long-range nature of the interelectron interaction, as the defect concentration δ in both situations is far below the percolation threshold.

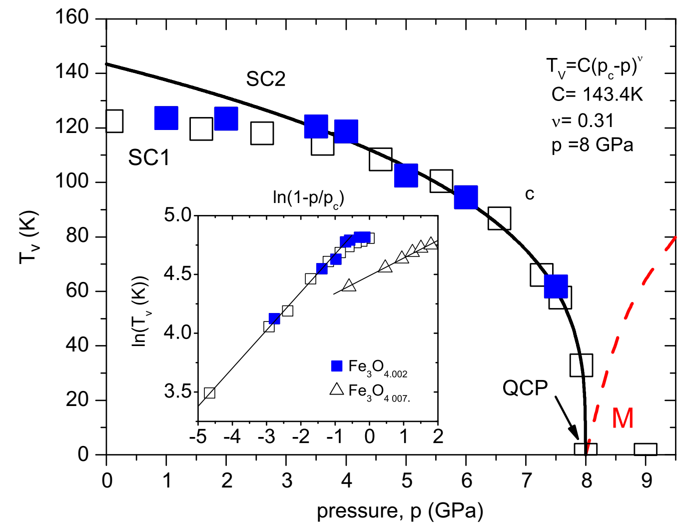

Fig. 2. Pressure dependence of the Verwey transition temperature T_V. We mark the data points from our work as solid squares (blue online) and those of Môri et al. [1] by open squares. Solid line represents the fit specified and ending at quantum critical point QCP. Inset: same in the doubly logarithmic scale. Open triangles show the respective critical behavior for slightly non-stoichiometric ($\delta = 0.007$) 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. The dashed line represents the proposed additional line between the SC2 and M phases at $T > 0$ and $p > p_c$ (see main text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In Fig. 2 we have also drawn the dashed line specifying a hypothetical line between the high-temperature semiconducting state SC2 and the metallic M phases. This transition (or crossover) line must be present, since the Verwey transition is the first-order transition between the two semiconducting phases SC1 and SC2. The dashed line is only a qualitative characteristic, as it can begin at $p < p_c$. The *quantum critical point* is then the terminal point located at $(p = p_c, T = 0)$ for which the energy of the two configurations Fe^{2+} and Fe^{3+} becomes degenerate at $T = 0$. This observation allows for an interpretation of the resonating-electron dynamics $Fe^{2+} \leftrightarrow Fe^{3+} + e$ between the two configurations in terms of a spinless-fermion model, as discussed in the next section. Apart from that, a very interesting question concerns the magnetic moment value and the behavior in the metallic phase, as discussed elsewhere [2]. One should note also that since the magnetic susceptibility becomes flat for $p \geq p_c$, one expects that the Curie temperature is still well above the temperature range specified in Fig. 1. It is not known as yet if Hund's rule is broken at or above p_c.

In order to make our discussion of quantum criticality more complete, we have redrawn in Fig. 3 a dependence [6] of T_V as a function of off-stoichiometry parameters $\delta' = (\frac{4}{3})\delta$ and x for the magnetite zinc- and titan-magnetite, respectively. A well defined discontinuous to continuous Verwey transition as a function of off-stoichiometry parameters takes place at $x \approx 0.012$ [6]. The value of $T_V = 0$ should be achieved about $x \simeq 0.12$ if the behavior is linear in the whole range of x and δ'. It would be very interesting to study those non-stoichiometric compounds to see if the quantum criticality can still be observed and to what extent it will be influenced by the atomic disorder. The observation of the dependence of the character depicted in Fig. 2 also in this case would be reaffirming us that in the limit of a light doping the applied and the chemical pressures are equivalent. But then the critical values x_c and δ'_c should be substantially smaller than 0.1.

One interesting general feature of the phase diagram depicted in Fig. 2 should be mentioned. Namely, the V-shape regime above the critical point should be regarded as *a quantum semiconducting*