Pressure dependence of electrical conductivity in $FeTiO_3$ Ilmenite

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Ilmenite is one of the main magnetic materials in nature. Ilmenite-type oxides (general formula ABO_3) are widespread and interest in material science, crystal chemistry and geosciences. They are often found in natural minerals from the Earth's interiors. Therefore, the structural change of ilmenite under pressure is thus useful for understanding in the Earth's mantle. Along with ilmenite, $FeTiO_3$ can form two other polymorphs: perovskite and lithium niobate ($LiNbO_3$) [1]. The structures of ilmenite and $LiNbO_3$ are closely related and are characterized by different orderings of the A and B cations.

The ilmenite structure was reported [2] and studied at high pressure and temperature [3]. The polymorphs are theoretically predicted at high pressures [4]. Ilmenite naturally occurs and is the most stable polymorph at ambient conditions. The ilmenite structure is based on an oxygen hexagonal-close-packed lattice with metal atoms, which occupy two-thirds of the available octahedral sites and form honeycomb-like layers of edge-shared octahedra.

Furthermore, $FeTiO_3$ undergoes phase transitions from the ilmenite phase to the perovskite phase at pressures above 20 GPa. The perovskite phase transforms to $LiNbO_3$ phase upon decompression [5]. A variety of charge and spin states induce a complicated phase diagram involving magnetic, electronic, and structural transitions.

The electrical resistivity measurement of ilmenite $FeTiO_3$ at high pressures and/or at high temperatures is a significant subject to understand the electronic state. Andreozzi *et al.* performed conductivity measurements on synthetic $FeTiO_3$ and natural ilmenite at high temperatures and at different oxygen partial pressures [6]. The pressure dependence of the resistivity has been studied [7] using synthetic ilmenite samples. The electrical conductivity of $FeTiO_3$ ilmenite has been reported at both high pressure and high temperature [8]. The electron density distribution of $FeTiO_3$ ilmenite was clarified under high pressure through maximum entropy method (MEM) using single-crystal diffraction intensities, and the anisotropic electrical conductivity was proposed. And, electrical resistance measurements of polycrystalline samples of $FeTiO_3$ under pressure revealed that $FeTiO_3$ becomes more conductive as the pressure increases [9]. However, the observed resistance is averaged in the bulk powder sample. Therefore, we aim to determine the pressure dependence of the resistivity and to elucidate the effect of anisotropic deformation of the crystal structure.

Ilmenite single crystals were synthesized using the floating method. Thin crystal plates parallel and perpendicular to the *c*-axis were prepared. We used a diamond anvil cell for pressure genaration. The pressure dependence of the resistance at room temperature was measured parallel and perpendicular to the *c*-axis. Pressures were determined using a ruby fluorescence system [10]. A mixture of c-BN and epoxy resin formed an insulating layer on the gasket. Alkaline metal halides (NaCl) were used as pressure media. Four Au electrodes were connected to the single-crystal sample.

Pressure dependence of electrical resistivity of ilmenite using on the oriented sample in the directions parallel and perpendicular to the *c*-axis up to 11 GPa at ambient temperature is presented in Fig. 1. Axial anisotropic conductivity under high pressure is observed.

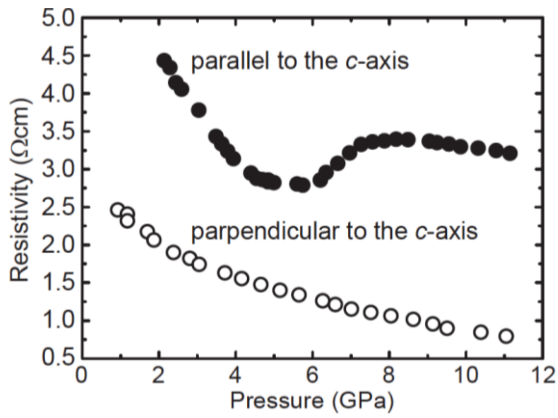

Figure 1. Pressure dependence of the resistances parallel and perpendicular to the *c*-axis.

The resistivity perpendicular to the *c*-axis continuously decreased with pressure. On the other hand, the resistivity along the *c*-axis initially decreased with pressure and under further compression, it increased with pressure. The resistivity maximum was observed at approximately 8 GPa. The observed resistivity behavior indicates super-exchange of electron hopping and consistent with the anisotropic electron density distribution observed by MEM using single crystal X-ray diffraction data[9].

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[1] F. Rodi, D. Bavel, Z. Anorg, Allg. Chem. 1965, **17,** 336.
[2] J. D. Barth, E. Posnjak, Z. Kristallogr. 1934, **A88**, 265.
[3] B. A. Wechsler, C.T. Prewitt, Am. Mineral. 1984, **69,** 176.
[4] N. C. Wilson, S. P. Russo, J. Muscat, N. M. Harrison, Phys. Rev. B 2005, **72,** 024110.
[5] L. C. Ming, Y. H. Kim, T. Uchida, W. Wang, M. Rivers, Am. Miner. 2006, 91, 120.
[6] G. B. Andreozzi, F. Cellucci, D. Gozzi, J. Mater. Chem. 1996, **6**, 987.
[7] C. Boekema, F. van der Woude, G. A. Sawatzky, J. Phys.Colloq. 1976, **37,** c-603.
[8] B. Zhang, T. Katsura, A. Shatskiy, T. Matsuzaki, X. Wu, Phys. Rev. B 2006, **73**, 134104.
[9] T. Yamanaka, Y. Komatsu, H. Nomori, Phys Chem. Minerals 2007, **34,** 307.
[10] H. K. Mao, J. Xu, P. M. Bell, J. Geophys. Res. 1986, **91**, 4673.