Geophysical Research Abstracts
Vol. 20, EGU2018-2257, 2018
EGU General Assembly 2018

Sensitivity of the Verwey Transition to Nonhydrostatic Stress

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When a crystal of pure magnetite is cooled below the Verwey temperature, Tv = 124 K, its lattice undergoes a small, reversible, nearly rhomohedral transformation strain as its crystal structure changes from cubic to monoclinic, its electrical conductivity drops two orders of magnitude, and its magnetocrystalline anisotropy increases by two orders of magnitude. The change in volume accompanying this first-order phase transition is relatively small because the increase due to stretching of the lattice along the body diagonal is partially counterbalanced by contraction at right angles to it. Thus the Clapeyron slope of the transition with pressure is small, dTv/dP = −3.7 K/GPa, compared to the thermodynamically calculated slopes of the phase boundary for the principal compressive stresses, dTv/dσ = −23.3, +10.8 and +8.8 K/GPa.

The phase-boundary slope under nonhydrostatic stress that will actually be observed, however, is complicated by the existence of twelve distinct monoclinic twin orientations relative to the cubic host, each with its own principal-stress slopes. If all of the twins are free to form–i.e. none is prevented from forming by external constraints–then the twin that is thermodynamically favored to form during cooling is the twin with transformation strain most compatible with the imposed stress. This is also the twin with the highest Verwey temperature, leading to the interesting conclusion that any nonhydrostatic component of stress in an experiment tends to raise Tv even though hydrostatic pressure lowers Tv. For instance, uniaxial stress, whether compressive or tensile, always raises Tv, ranging up to six times more per gigapascal than with hydrostatic pressure, depending on orientation. This conclusion helps explain the puzzling scatter of experimental results for dTv/dP in the literature, in particular the large positive value of 16 K/GPa observed in 2007 by Nasagawa et al. during compression of a magnetite single crystal parallel to [110].