Effect of Electronic Disordering on the Thermal Equation of State of Magnetite

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Magnetite is technologically and scientifically important by virtue of its unique magnetic and electrical properties. It is a common mineral found in a variety of geologic environments, and plays an important role in deciphering the oxygen evolution in the Earth’s atmosphere and deep interiors. This application requires the knowledge of the thermal and elastic properties of magnetite at high pressures and temperatures. Such information, however, is lacking in literature. Furthermore, it’s known that magnetite experiences electronic disordering at high temperature and ambient pressure, resulting in its anomalous thermal expansion. Such processes will undoubtedly complicate the determination of and affect the thermal equation of state of magnetite.

We have carried out in-situ diffraction experiments on magnetite using synchrotron radiation at beamline X17B2 of National Synchrotron Light Source (NSLS-I) and 6-BM-B of Advanced Photon Source (APS). A D-DIA module in a 250- or 1100-ton hydraulic press and WC anvils were employed for compression, and diffraction spectra were collected at simultaneous high pressures ($P$) and temperatures ($T$) (up to 9 GPa and 900 °C). Mixture of amorphous boron and epoxy resin was used as pressure medium, and NaCl as pressure marker. Temperature was recorded by type-D thermocouples. It is found that, when pure magnetite was used as sample, the electronically disordered states at high $T$ (> 500 °C) are at least partially quenchable to room $T$ at high pressures, which has never been observed at ambient pressure. The room-$T$ data define an “apparent” bulk modulus for magnetite that is about 10% smaller than the generally accepted values. The surprising sluggishness of the electronic order-disorder also resulted in the delay of magnetite reaching the equilibrium states at lower temperatures ($T < 500$ °C). However, when a mixture of magnetite and NaCl was used as the starting sample, equilibrium order-disorder state was achieved at all $P – T$ conditions, and same experimental procedure yielded a room-$T$ bulk modulus for magnetite in agreement with literature data. Hence the sluggishness observed in pure magnetite sample is not due to the high pressure, but rather perhaps the deviatoric stress generated during cooling. It’s evident that, when two pressure-volume datasets at room $T$ are compared, the electronic disordering in magnetite is suppressed by pressure and ceases to operate at pressures higher than 6 - 7 GPa, which is in accordance with the thermodynamics of the order-disorder deduced from diffraction data at high temperature and ambient pressure.