High-pressure and high-temperature equation of state of cobalt oxide: Implications for redox relations in Earth’s mantle

MATTHEW M. ARMENTROUT,* EMMA S.G. RAINNEY, AND ABBY KAVNER

Department of Earth and Space Science, University of California Los Angeles, Los Angeles, California 90095, U.S.A.

ABSTRACT

The high-pressure and high-temperature equation of state of rock salt-structured cobalt oxide was measured up to 65 GPa and 2600 K using synchrotron X-ray diffraction in conjunction with the laser heated diamond-anvil cell. Fitting a Mie-Grüneisen-Debye model to the data we find best-fit parameters $V_0 = 77.4$ (fixed) Å$^3$, $K_0 = 190$ (1) GPa, $K' = 3.49$ (4), $\gamma_0 = 1.54$ (4), $q = 2.87$ (15), and $\Theta_\mathrm{b} = 517.8$ K (fixed). We use this newly determined equation of state in conjunction with existing measurements of the thermoelastic parameters of cobalt metal to calculate the Gibbs free-energy difference between the cobalt oxide and cobalt metal phases as a function of pressure and temperature. A comparison of the energetics of the Co/CoO system with the Ni/NiO system predicts that below 58 GPa CoO+Ni is stable relative to NiO+Co, while above 58 GPa the reverse is true. This tipping point in energy can be mapped as a crossing point in the electrochemical potential of the two metal ions, suggesting that cobalt becomes more siderophile than nickel with increasing pressure. This result is in qualitative agreement with existing measurements of nickel and cobalt partition coefficients between mantle and core materials.

Keywords: Synchrotron X-ray diffraction, cobalt oxide, equation of state, high pressure, thermoelastic properties, diamond-anvil cell, laser heating, redox

INTRODUCTION

First row transition metals play important roles in the Earth’s mantle by influencing phase stability, density, and elastic properties, and helping to govern defect-mediated behavior including electrical and thermal conductivity and rheology. Since transition metals are also somewhat siderophile, geochemical measurements of absolute and relative abundances of transition metals in mantle-derived rocks help constrain the evolution of the core/mantle system, including initial segregation and continuing reactions. Understanding the transition metals’ roles in deep Earth transport properties and interpreting the geochemical record in terms of partitioning of transition metals among oxide, silicate, and metal phases requires a suite of measurements at the high-pressure and -temperature conditions of the mantle, including their thermoelastic equation of states, phase stability, and partitioning behavior.

In particular, the partitioning of cobalt and nickel between reduced metallic core material and oxide/silicate phases has been measured and used to predict the conditions of an early core/mantle boundary (Bouhifd and Jephcoat 2011; Kegler et al. 2008; Li and Agee 1996, 2001; O’Neill et al. 1998; Righter 2003; Siebert et al. 2012; Tschauner et al. 1999). However, at pressures and temperatures corresponding to the lower mantle, partitioning measurements become increasingly difficult to make in ultrahigh-pressure devices such as the diamond-anvil cell due to the small sample sizes, large temperature gradients, and lack of control over the chemical environment, especially oxygen fugacity. An alternate path to predicting the redox tendencies of metal/oxide systems in the deepest part of the Earth’s mantle is to measure the thermoelastic properties directly at the temperatures and pressures relevant to the Earth’s mantle, and use these values to calculate relative free energies of redox reactions at extreme conditions (e.g., Campbell et al. 2009). While equation of state measurements exist for the Fe/FeO and Ni/NiO systems (Campbell et al. 2009), the phase stability and equation of state of cobalt oxide has not been studied at simultaneous high pressure and temperature.

In addition, insulating solids containing transition metal oxides are used in various applications that take advantage of their highly correlated electron behaviors. Therefore, there has been some community effort to understand the behavior of transition metal oxides, including cobalt oxide, at high pressure. At ambient conditions, cobalt oxide adopts a paramagnetic rock salt structure, and, like several other transition metal oxides, it undergoes a slight combined rhombohedral and tetragonal distortion to an antiferromagnetic phase below its Néel temperature (Wdowik and Legut 2008; Roth 1958; Shull et al. 1951). The bulk modulus of the B1 phase of cobalt oxide has been measured both by ultrasonic (Sumino et al. 1980) and static (Guo et al. 2002) methods and its ambient-pressure thermal expansion has been measured (Massobrio and Meyer 1991; Touzelin 1978). Cobalt oxide shows a pressure-induced distortion to the rhombohedral phase at 43(2) GPa (Guo et al. 2002). At 90–97 GPa, cobalt oxide undergoes a volume collapse that is associated with a high- to low-spin transition similar to ferropericlase (Guo et al. 2002; Rueff et al. 2005; Zhang et al. 2009).

To enrich our mineral physics understanding of transition metal oxide behavior at simultaneous high pressures and tem-