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

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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), γ_0 = 1.54 (4), q = 2.87 (15), and θ_0 = 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