American Mineralogist, Volume 97, pages 399–406, 2012

Variations in elastic and anelastic properties of Co_3O_4 due to magnetic and spin-state transitions

ZHIYING ZHANG,[1,*] JOHANNES KOPPENSTEINER,[2] WILFRIED SCHRANZ,[2] AND MICHAEL A. CARPENTER[1]

[1]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.
[2]Faculty of Physics, University of Vienna, Strudlhofgasse 4, A-1090, Vienna, Austria

ABSTRACT

Elastic anomalies and acoustic dissipation associated with spin-state transitions of Co^{3+} in Co_3O_4 have been investigated using resonant ultrasound spectroscopy (RUS) at high frequencies (0.1–1.5 MHz) between 6 and 1107 K, and dynamic mechanical analysis (DMA) at low frequencies (0.1–50 Hz) between 127 and 775 K. Above ~800 K, the shear modulus decreases with increasing temperature and the acoustic dissipation increases. The amount of softening scales linearly with an empirical order parameter for low spin → low spin + high spin states derived from analysis of changes in unit-cell volume with temperature. The mechanism for anelastic losses is not understood but must be due to relaxation of strains coupled either to changes in spin state or to changes of cation configuration between tetrahedral and octahedral sites occurring by electron exchange. The pattern of shear modulus softening, in proportion to the spin order parameter, is likely to be general for cubic structures containing cations, which undergo spin-state transitions, such as Fe^{2+} in (Mg,Fe)O. Below ~30 K, RUS data show a large softening of the shear modulus and a steep increase in acoustic dissipation due to the magnetic transition from paramagnetic to antiferromagnetic. This could be understood in terms of the influence of a symmetry breaking strain coupled to the magnetic order parameter such that cubic lattice geometry is not maintained. Possible magnetic space groups for the antiferromagnetic structure are considered through the use of the group theory.

Keywords: Phase transition, spin state, resonant ultrasound spectroscopy, dynamic mechanical analysis