Antiferromagnetic nanoparticles

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Nanoparticles of antiferromagnetic materials such as α-Fe_2O_3 (hematite), α-FeOOH (goethite) and ferrihydrite, commonly found in geological environments, have attracted limited attention in magnetic studies, because the sublattice magnetizations are aligned antiparallel such that the particles may have negligible magnetic moments. A number of studies have, however, revealed that antiferromagnetic nanoparticles have a wealth of fascinating magnetic properties, e.g. a magnetization due to uncompensated spins with implications for their rock magnetic signature [1]. Recently we proposed that the thermal energy may excite the magnetic structure of antiferromagnetic nanoparticles such that a thermoinduced magnetic moment occurs [2]. This is a novel type of nano-magnetism where the magnetization increases with temperature. At room temperature the thermoinduced magnetic moment can be similar in magnitude to that originating from uncompensated spins. Magnetic dipole interactions between antiferromagnetic nanoparticles can be considered negligible [3-5] despite magnetic moments from e.g. uncompensated spins, but strong exchange interactions can be established between surface atoms of neighboring particles by drying aqueous suspensions of particles [3-5]. This interparticle exchange interaction significantly influences the properties of the individual particles [3-5] e.g. it suppresses superparamagnetic relaxation. In samples with strong interactions, there is a tendency for oriented attachment of the particles [4]. It is possible that exchange interaction can act as a driving force for the attachment. The agglomeration process is reversible, in the sense that ultrasonic treatment or grinding can separate the particles and reinduce fast superparamagnetic relaxation without reducing particle sizes [4,6]. Thus the nanoscopic coupling between particles is sensitive to simple macroscopic treatments. The results stress that the properties of nanoparticles, in addition to differing from bulk properties, have to be described in terms of interactions.

References

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In situ observation of thermodynamic size effects on melting of natural gold nanoparticles

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Thermodynamic and quantum size effects, i.e. the change in physical and electronic properties as size is decreased to the nanoscale, are widely documented for synthetic nanomaterials. However, there is little information on how natural nanocrystalline materials behave under a wide range of geological temperatures. In order to evaluate size effects on melting of metal nanoparticles, we have performed controlled heating experiments of natural gold nanoparticles in As-rich pyrite (formed at ~150-200°C) under HAADF-STEM observation.

In-situ heating in the TEM revealed no changes in the initial size distribution until ~350°C, where the smallest nanoparticles (<2 nm) start to melt. The most dramatic changes in nanoparticle size and distribution occur between 400-500°C; nanoparticles with diameters <2 nm melt completely at ~440°C, while at temperatures above 500°C, only nanoparticles >8 nm in size are stable. Computer-aided HAADF image analysis of size distributions as a function of temperature reveal that the initial average diameter (~4 nm) of Au nanoparticles is constant until ~350°C, above which it starts to increase gradually. The increase in average size is coupled with a significant decrease in the number of nanoparticles as temperature is raised above 400°C. At 600°C, the upper temperature bound of the experiment, only 3 nanoparticles (~25 nm) have survived, replacing the initial 115 of average size ~4 nm. During heating, larger nanoparticles (~9 nm) grow at the expense of the smaller ones (<2 nm) although no coalescence is observed.

Analytical results reveal that a significant fraction of the initial size distribution of Au nanoparticles (~2-8 nm) is unstable at temperatures above ~350°C, confirming thermodynamic size effects on melting in natural samples. As a result, the preservation of metallic gold nanoparticles in the geologic record is size-dependent, and restricted to lower temperature (<400°C) hydrothermal systems.