Giant Negative Thermal Expansion in Magnetic Nanocrystals

Most solids expand when they are heated but a property known as negative thermal expansion (NTE) has been observed in a number of materials, including the oxide ZrW_2O_8 [1] and the framework material $Zn_xCd_{1-x}(CN)_2$ [2]. This unusual behaviour can be understood in terms of low-energy phonons, while the colossal values of both positive and negative thermal expansion recently observed in another framework material, $Ag_3[Co(CN)_6]$, has been explained in terms of the geometric flexibility of its metal-cyanide-metal linkages [3]. Thermal expansion can also be stopped in some magnetic transition metal alloys below their magnetic ordering temperature, a phenomenon known as the Invar effect, and the possibility of exploiting materials with tunable positive or negative thermal expansion in industrial applications has led to intense interest in both the Invar effect and NTE.

Here, we report our recent finding of giant negative thermal expansion in magnetic nanocrystals of CuO and MnF_2 [4]. The cupric oxide, CuO, is a unique transition metal monoxide that was clarified by us to show strong charge-spin-lattice coupling and ferroelectric properties below its magnetic (antiferromagnetic) transition [5]. This strong charge-spin-lattice coupling has recently received intense attention and has been renamed with the term "multiferroics." Our previous structure study suggested small anomalies in the lattice parameters at its magnetic transition temperature (Néel temperature T_N) and the disappearance of thermal expansion below T_N (i.e., zero thermal expansion). CuO fine particles with sizes narrowly distributed around ~5 nm were prepared by ball-milling from large (~cm) pure single crystals grown by a chemical vapor transport method. The high-resolution TEM image suggests that they are of crystalline nature (Fig. 1). A surprising result concerning the ball-milled nanoparticles is the absence of the lattice defects that one might expect from the balling process (as is the case in our ball-milled submicron particles (Fig. 1)).

The powder X-ray diffraction experiments were carried out at beamline **BL02B2** using a large Debye-Scherrer camera with an imaging plate. XRD data were collected at various temperatures from 300 K to 20 K with 0.01° steps from 0.00° to 75.00° for 2θ. The wavelength of the incident X-ray was tuned to approximately 0.5 Å using the Si double monochromator.

The lattice constants of the nanocrystals at various temperatures were analyzed by the Rietveld method. Nanoparticle CuO has the single crystal structure, as shown in Fig. 2. We found a large NTE effect ($\beta=-1.06\times10^{-4}K^{-1}$) for 5 nm nanocrystals of CuO below its magnetic ordering temperature (Fig. 3). By comparison the renowned NTE compound ZrW_2O_8 has $\beta=-2.6\times10^{-5}K^{-1}$ [1]. A similar result was observed for nanoparticles of MnF_2 but not for NiO. Larger particles

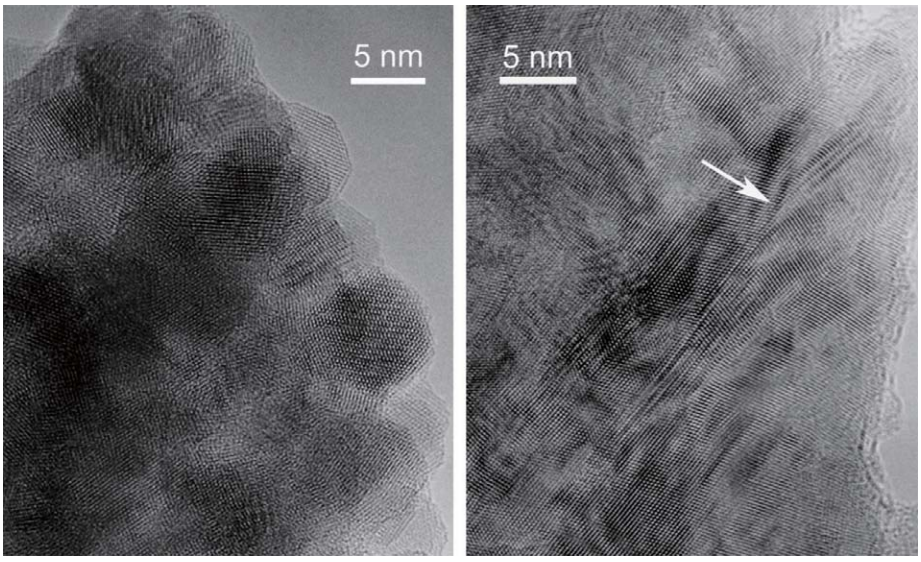

Fig. 1. Electron micrograph of nanocrystals (the left) and submicron particles of ball-milled CuO.

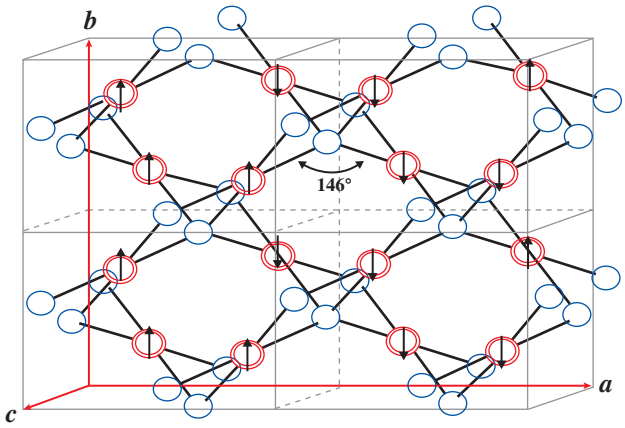

Fig. 2. Crystal structure of CuO. The arrows represent the ordered spins below its magnetic transition temperature.

of CuO and MnF_2 also show a prominent Invar effect below their magnetic ordering temperature constant, whereas this behavior is not observed in NiO. We propose that the NTE effect in CuO (which is four times larger than that observed in ZrW_2O_8) and MnF_2 is a general property of nanoparticles in which there is strong coupling between magnetism and the crystal lattice, i.e., magnetostriction.

As is highlighted by Goodwin in Nature Nanotechnology [6], "if the link between magnetostriction and the NTE in nanoparticles proves to be general – and the materials science community will no doubt explore this possibility – then these results really are a very significant advance. Nearly all high-end functional materials show some form of magnetic ordering – this includes high-temperature superconductors, colossal magnetoresistance manganites and the rapidly expanding family of multiferroics. These are precisely the type of materials used in multicomponent devices, where compatibility between mechanical properties is paramount." Moreover, the present finding suggests that "the particle size affects their fundamental thermodynamics in nanocrystalline magnets. Particle size has always been an important variable in materials science, but now the field has a clear indication of how it might be used to vary – and even invert – the complex interdependencies among fundamental parameters such as temperature, pressure and magnetism. If these principles can be extended to multiferroic materials, where magnetic order and electric polarization are linked, one might hope to develop nanoscale switches and sensors with previously unimaginable electronic responses to changes in temperature or pressure."

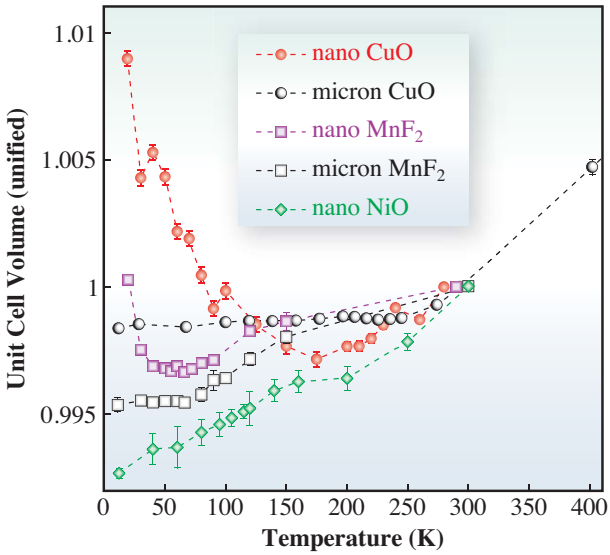

Fig. 3. Negative thermal expansion in nanocrystals of CuO and MnF_2, but not NiO. The unit cell volumes are normalized by their room-temperature values, respectively.

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