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# Size Effect of Charge Density Wave Phase Transformation in $EuGa_4$ Compound Nanoparticles

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Charge density wave (CDW) phase transformations are formation phenomena of long-range order phase induced by periodic modulated charge density at low temperature, and the electron-lattice interaction plays an important role in the behavior. It is known that the CDW phase transformation temperature in bulk $EuGa_4$ compound is 104 K under hydrostatic pressure more than 1 GPa [1]. If the system size decreases to nanometer scale, the periodic modulated structure changes by an electron confinement effect, and a high pressure state in the interior of a specimen is induced by a surface effect. In the present study, a size effect of CDW phase transformation in $EuGa_4$ compound nanoparticles has been studied by TEM.

Preparation of size-controlled $EuGa_4$ particles was carried out with the use of a double-source evaporator installed in the specimen chamber of an electron microscope. An amorphous carbon film was used as a supporting film and was mounted on a molybdenum grid. Using the evaporator, gallium was first evaporated from one filament to produce gallium particles on the supporting film, and then europium was evaporated from the other filament onto the same film. The supporting film was kept at ambient temperature during the deposition. Vapor-deposited europium atoms quickly dissolved into gallium particles to form $EuGa_4$ compound particles. Observations were carried out using the same microscope Hitachi H-9000 ultra-high vacuum TEM operating at an accelerating voltage of 200 kV. The electron flux used for excitations was $1.0 \times 10^{20}$ e $m^{-2}s^{-1}$. The temperature of particles on the supporting films was kept at 293~16K by liquid He specimen holder during the experiments. Structural changes associated with cooling were observed in situ by bright-field images (BFIs) and selected-area electron diffraction patterns (SAEDs).

$EuGa_4$ nanoparticles less than approximately 80 nm in diameter at 298 K have the tetragonal structure with the lattice constants of a=0.44 nm and c=1.61 nm, and the value of lattice constant of the c axis in nanoparticles is different from that in bulk compound (a=0.44 nm, c=1.07 nm) [1]. In approximately 80 nm-sized nanoparticles, when the specimen temperature is decreased to 16~32 K, no structure changes. Figures 1(a) and (b) show SAEDs of $EuGa_4$ nanoparticles with average particle size of about 20 nm at 298 K and 32 K, respectively. At 298 K, the SAED pattern is indexed as Debye-Scherrer rings of $BaAl_4$ type body tetragonal with lattice constant a=0.44 nm, c=1.61 nm. On the other hand, when the specimen temperature is decreased to 32 K, the structure has changed to the orthorhombic structure containing a $\sqrt{2} \times \sqrt{2}$ ordered structure with lattice constants of a=0.44 nm, b=0.45 nm and c=1.61 nm.

This result indicate that CDW phase transformation at a low temperature is induced with decreasing size in $EuGa_4$ nanoparticles. The lattice structure of $EuGa_4$ compound consists of the 2 dimensional layers by europium atoms and the hard cage structure by gallium atoms. At low temperature, local atomic displacements of europium atoms due to CDW destroy the lattice symmetry and the orthorhombic structure was induced. From the results, it is suggested that the CDW phase transformation takes place in $EuGa_4$ nanoparticles. The reason why CDW phase transformation is induced in $EuGa_4$ nanoparticles

below a critical size is attributed by surface effects. As estimated in Figure 2, with decreasing size, pressure in the interior of a nanoparticle will increase depending on Young–Laplace equation [2]. A synergy effect of the pressure difference and lattice softening in approximately 20 nm-sized particles may enhance CDW phase transformation at low temperature.

References:

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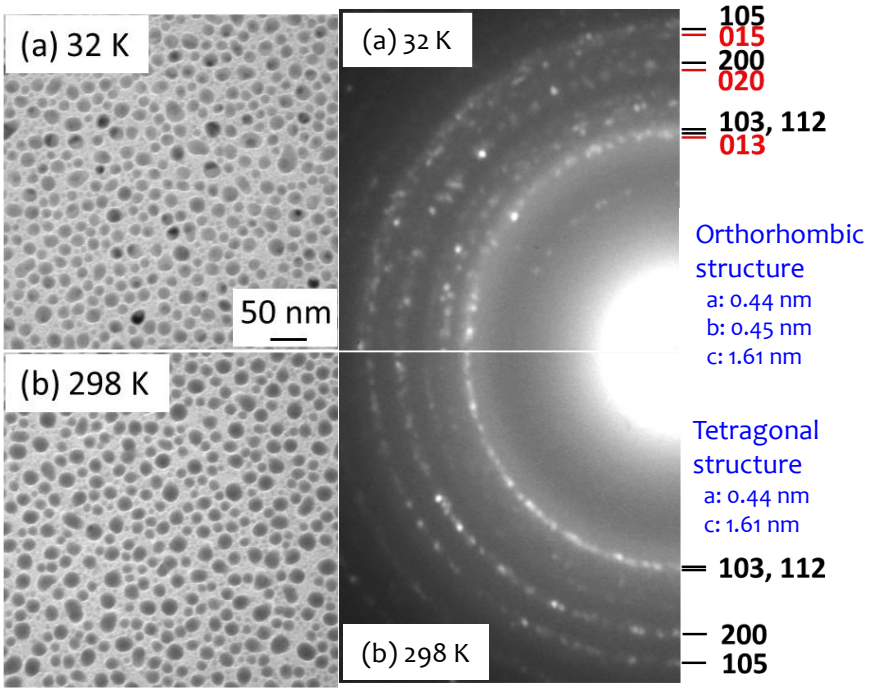


**Figure 1.** (a) and (b) show SAEDs of $EuGa_4$ nanoparticles with average particle size of about 20 nm at 298 K and 32 K, respectively.

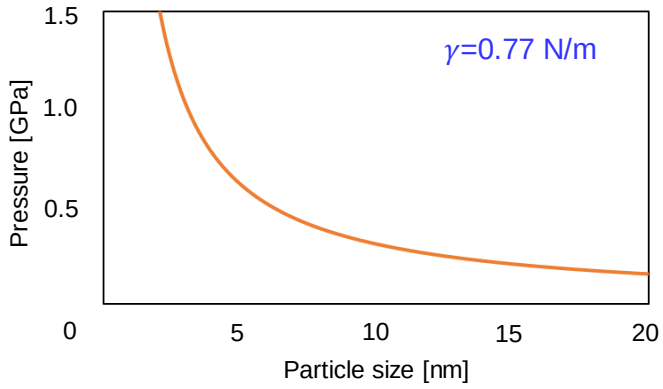


**Figure 2.** Pressure difference depending on Young–Laplace equation in $EuGa_4$ nanoparticles.

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