Thermal Contraction of Au Nanoparticles


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(Received 17 April 2002; published 5 September 2002)

A fine Au powder, with a mean particle diameter of 4 nm, has been successfully fabricated. The crystalline structure of the 4 nm Au nanoparticles remains in fcc symmetry. No structural changes were found between 15 and 450 K. A crossover from a positive thermal expansion at low temperatures to a negative thermal expansion at high temperatures was observed in the fcc cell parameter at about 125 K. Anomalies associated with the crossover were also observed in the magnetic response and the heat capacity measurements. The observations can be reasonably well interpreted by accounting for the effects of the valence electron potential on the equilibrium lattice separations, with a weakly temperature dependent level spacing.

DOI: 10.1103/PhysRevLett.89.135504 PACS numbers: 81.07.Wx, 81.16.Be, 85.85.+j

Thermal expansion is normally observed in most materials. This behavior can be understood by accounting for the effects of the anharmonic lattice potential on the equilibrium lattice separations and is usually characterized by the Grüneisen parameter [1] in terms of a linear expansion coefficient, \( \alpha = \frac{1}{a} \frac{\partial a}{\partial T} \), where \( a \) is the lattice parameter. Negative thermal expansion, which represents lattice contraction upon heating, is not uncommon among anisotropic systems, where contraction along one crystalllographic direction is usually accompanied by expansion along the others [2]. For isotropic systems, it is frequently associated with a structural distortion related to anisotropic lattice excitations [3]. In most cases, negative thermal expansion occurs in only a narrow temperature range. In this Letter, we report on the observation of a crossover from a positive thermal expansion at low temperatures to a negative thermal expansion at high temperatures in cubic Au nanoparticles, where no structural changes have occurred.

Au nanoparticle powder was fabricated by employing the gas condensation method. High-purity gold ingots (99.999\%) were evaporated in an Ar atmosphere at a pressure of 0.8 torr, using an evaporation rate of 0.1 Å/s. A stainless steel plate, maintained at the liquid nitrogen temperature, was used to collect the evaporated particles. After restoration to room temperature, the powder, which is only loosely attached on the collector, was stripped off. The resultant powder was no longer gold yellow but dark black, indicating that the absorption band of the powder had blueshifted to the invisible region, as most metallic nanoparticles do. The sample was in a powder form, consisting of a collection of individual Au nanoparticles. There is no substrate. The sample was quite stable against exposure to the air, but was sensitive to heat. However, the data shown in this Letter were all obtained on the sample that was kept in isolation from the air at all times.

X-ray diffraction and atomic force microscopy (AFM) were used to characterize the powder. Figure 1(a) shows the x-ray diffraction pattern of the powder (bottom) and of the ingot used for evaporation (top). As expected, the diffraction peaks of the powder are much broader than those of the ingot, reflecting the finite-size effect. A portion of the AFM images and the size distribution, obtained from a 1 \( \mu \)m \times 1 \( \mu \)m image, are shown in

![Figure 1](image)

**FIG. 1.** (a) The x-ray diffraction patterns, taken at room temperature, of the nanoparticles and the ingot. Line broadening, resulting from the finite-size effect, can be clearly seen in the nanoparticle pattern. The inset shows the observed (circles), fitted (solid curve), and instrumental resolution (dashed curve) profiles for the \{111\} reflection. (b) A portion of an AFM image of the nanoparticle powder. A symmetrical size distribution is obtained which may be described by using a Gaussian distribution function, indicated by the solid curve.
Below 100 K, a positive thermal expansion is seen, with a linear expansion coefficient of \( \alpha = +3.2 \times 10^{-5} \text{ K}^{-1} \). Above 150 K, the linear expansion coefficient becomes negative (\( \alpha = -2.5 \times 10^{-5} \text{ K}^{-1} \)), showing lattice contraction, rather than expansion, upon heating. Note that normal positive thermal expansion was observed \([9, 10]\) in nanoscale Au grains deposited on carbon substrate. In these so-called “island film” systems, the interactions between the grains and the substrate can be important, which may result in a weakening of the apparent size effects of the grains themselves.

Below 400 K, a positive thermal expansion is observed, with a linear expansion coefficient of \( \alpha = +2.5 \times 10^{-5} \text{ K}^{-1} \). Above 400 K, the linear expansion coefficient becomes negative (\( \alpha = -2.5 \times 10^{-5} \text{ K}^{-1} \)), showing lattice contraction, rather than expansion, upon heating. Note that normal positive thermal expansion was observed \([9, 10]\) in nanoscale Au grains deposited on carbon substrate. In these so-called “island film” systems, the interactions between the grains and the substrate can be important, which may result in a weakening of the apparent size effects of the grains themselves.

Below 100 K, a positive thermal expansion is seen, with a linear expansion coefficient of \( \alpha = +3.2 \times 10^{-5} \text{ K}^{-1} \), which is a factor of 2.3 times larger than that of the bulk Au (\( \alpha = +1.4 \times 10^{-5} \text{ K}^{-1} \)) \([8]\), signifying the existence of effects due to excitations other than from the lattice. A downturn in the temperature dependence of the cell parameter occurs at about 125 K. Above 150 K, the linear expansion coefficient becomes negative (\( \alpha = -2.5 \times 10^{-5} \text{ K}^{-1} \)), showing lattice contraction, rather than expansion, upon heating. Note that normal positive thermal expansion was observed \([9, 10]\) in nanoscale Au grains deposited on carbon substrate. In these so-called “island film” systems, the interactions between the grains and the substrate can be important, which may result in a weakening of the apparent size effects of the grains themselves.

The above observations can be described reasonably well by accounting for the effects of electronic excitations on the equilibrium lattice separation. For bulk systems, where the band separations near the Fermi surface are considerably larger than the thermal energy (a few meV), the electronic effects become noticeable only at relatively high temperatures. In nanoparticles, where discrete levels are separated by only a few meV \([11–13]\), the effects can be significant even at ordinary temperatures. Here, we consider the effects of the valence electron potential on the equilibrium lattice separation in systems (specifically for nanoparticles) having discrete electronic energy levels.
levels. It is known that the allowed energies for valence electrons in nanoparticles can be taken as being inversely proportional to the cube of the particle diameter, which may vary with temperature. A temperature dependent level spacing is then to be anticipated for these spatially confined valence electrons. In terms of the unit cell parameter \( R(T) \), the energy of the \( n \)th level above the Fermi energy, for a cubic crystalline structure, may then be taken to be \( \Delta_n(T) = \alpha_n/R^3 \), where \( \alpha_n \) depends on the distribution of the levels \([11]\). Accordingly, the attractive binding energy of thermally excited valence electrons embedded in a cubic lattice of ions, at a finite temperature, is taken to be approximately \( U_n = -N_c \sum_n \Delta_n(R)f(\Delta_n) \), where \( N_c \) is the number of valence electrons and \( f(\Delta_n) = \frac{\exp(-\Delta_n/kBT)}{\sum\exp(-\Delta_n/kBT)} \) is the Fermi-Dirac population function of the \( n \)th level. The requirement of an energy minimum for equilibrium atomic separations reads \( \left( \frac{\partial^2 U_n}{\partial R^2} \right)_{R=R_0} = 0 \), where \( U_0 \) is the electrostatic energy of the metallic nanoparticles at \( T = 0 \) and \( a \) is the equilibrium lattice constant. Apparently, the second term accounts for the correction of the valence electron energy on the equilibrium lattice positions. It originates from the binding potential of the excited valence electrons in the electrostatic field of the ion cores. Figure 4 shows the variation of the second term with temperature, for an equal spacing (\( \Delta_n = n\Delta \)) ten-level system \([14]\). A minimum occurs at \( T_{\text{min}} = 2.19\Delta/k_BT \), indicating that the effects on the lattice parameters are different for temperatures below and above \( T_{\text{min}} \). A crossover from a positive thermal expansion to a negative thermal expansion can then be anticipated at \( T = 2.19\Delta/k_BT \). Another characteristic temperature of interest is \( T_0 = 4.05\Delta/k_BT \), at which \( dU_n/dr = 0 \). This is the temperature at which \( U_n \) reaches its maximum, but no correction to the equilibrium lattice positions from the excited valence electrons is made.

For the data shown in Fig. 2, we believe, however, that both the lattice and the valence electrons will contribute to the thermal behavior of the cell parameter. Unfortunately, no data on the lattice expansion coefficient of Au nanoparticles is available. As a reasonable estimate, we adopt the expansion coefficient of the ingot \([8]\) for that of the nanoparticle. The inset of Fig. 4 shows the temperature dependence of \( 1/a^2 \), where \( a^2 \) is the cell parameter corrected for the lattice contribution by using a linear expansion coefficient of \( 1.4 \times 10^{-5} \text{ K}^{-1} \). The solid line indicates the theoretical curve for \( \Delta = 3.5 \text{ meV} \), taking the data obtained at the lowest temperature as the reference point for \( dU_0/dr \). This value of \( \Delta = 3.5 \text{ meV} \) obtained for 4 nm Au particles agrees well with the 3.24 meV predicted by using Kubo theory \([10,15]\). We remark that using a temperature dependent \( \Delta \) in the fit produces essentially no difference in the results, since the variation of \( \Delta \) with temperature is \( \sim 1\% \), according to the data shown in Fig. 2.

Knowing that the paramagnetic response is proportional to the difference between the spin-up and the spin-down populations, it is reasonable to expect that the maximum paramagnetic response will appear at the temperature at which the thermally excited population reaches its maximum. This temperature can be taken to be at \( T = T_0 = 4.05\Delta/k_BT \), because the variation of \( \Delta \) with temperature is only \( \sim 1\% \) and the maximum population and the maximum \( U_n \) should occur at essentially the same temperature. Using the same \( \Delta = 3.5 \text{ meV} \approx 40.6 \text{ K} \) as that obtained from the cell parameter data, the maximum paramagnetic response will then be expected

FIG. 3. (a) Temperature dependence of the magnetic response of the Au nanoparticles and the ingot to a weak ac probing magnetic field. Diamagnetic responses for the ingot can be noted, while paramagnetic responses, with a clear peak at about 160 K, are revealed for the nanoparticles. (b) Variation of the heat capacity of Au nanoparticles with temperature. Two anomalies are clearly revealed in the \( dC/dT \) versus \( T \) plot shown in the inset.
to be at $40.6 \times 4.05 = 164$ K, which agrees very well with the data shown in Fig. 3(a).

Thermal lattice contractions originating from structural changes have been observed in many systems [16,17]. This is, however, not what occurs in the present 4 nm fcc Au nanoparticles, since no structural changes were observed in the temperature regime studied. Lattice shrinking results in an increase in the level separation when the temperature is increased, which, on the one hand, reduces the number of electrons occupying the excited states as dictated by the Fermi-Dirac factor and, on the other hand, raises the thermal energy of individual electrons in the excited states. These two factors compete delicately to achieve a lower electronic potential energy that results in the crossover from thermal expansion to thermal contraction. There may possibly be other effects that might be just as significant. Effects resulting from surface stress, from surface phonons, from finite-size modified lattice potential can all be significant in nanoparticles. Further theoretical investigations along these lines are needed to clarify their effects on the equilibrium lattice separations.

This work was supported by the National Science Council of the Republic of China under Grants No. NSC 90-2112-M-008-043 and No. NSC 90-2112-M-008-045.


[14] Ten levels above the Fermi level are included in the calculation, so that the population at higher levels is less than 3% even at the temperature with $k_BT = 3\Delta$.