Structure and vibrations of chemically produced Au_{55} clusters

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We performed optical absorption and temperature-dependent extended x-ray-absorption fine-structure (EXAFS) measurements on 55-atom gold clusters made by the Schmid process. The results are consistent with a fcc cuboctahedron structure, but with first-neighbor distances contracted by 0.075 Å. The electronic properties, as detected by optical and x-ray absorption, are as expected for a small chunk of gold. The EXAFS Debye-Waller factor shows that the clusters have 40% less thermal vibration than does the bulk. We present a theory for this effect, based on the change of bulk modulus with volume, the measured contraction of the clusters, and the softening effect of the surface modes.

I. INTRODUCTION

Clusters containing 10–1000 atoms have been of much interest as representatives of the transition between molecules and small bits of solid.[1,2] It is in this size region that such collective properties as metallic behavior, plasmons, and melting are expected to appear. However, it is hard to obtain monodisperse samples of materials in this size range, in part due to the tendency of small particles to aggregate if not protected by surface coatings.

Au clusters have been important test cases for phenomena at the cluster scale. Properties such as melting,[3] optical absorption,[4] and thermal vibration[5] have been studied. However, most of these studies have relied on material prepared by evaporation, which tends to be polydisperse, especially at small sizes. In contrast, Schmid showed that one can prepare monodisperse 55-atom Au clusters by chemical means,[6] and that the ligands with which these clusters are naturally equipped allow macroscopic amounts of cluster material to be kept together without fear of aggregation.

Schmid used a variety of indirect probes to propose a structure for this cluster: a cuboctahedron of Au with Cl atoms on each of the six (200) faces, and triphenylphosphine groups at each of the 12 (112) corners.[7] The bulky triphenylphosphine ligands protect the surface, allowing the cluster to remain unaggregated even with 24 of its 42 surface atoms unattached to any ligand. This low coverage, the ease of prepartion, and its stability to air and moisture make the Schmid cluster an ideal model of metallic behavior at small sizes.

In this paper, we report the results of a temperature-dependent extended x-ray-absorption fine-structure (EXAFS) investigation with supporting results from optical-absorption- and x-ray-absorption-edge studies. We find the results to be consistent with the view of this cluster as a strained, squeezed piece of fcc Au with ligands on it. Further, we find that the thermal vibrations of the cluster are less than those of bulk gold.

II. EXPERIMENT

The cluster was synthesized according to the method of Schmid,[6] in which $ClAuP(C_6H_5)_3$ in benzene is reduced by diborane. The reaction was carried out anaerobically, but the product was air-stable for long periods. Tetrahydrofuran (THF) solutions were made up fresh for optical spectroscopy. Optical spectra were taken with a diode-array spectrometer, and compared with spectra from the Au film left on the cuvette wall by decomposition of the cluster after long standing in solution.

To prepare EXAFS samples, we made a fresh THF solution of the cluster, then soaked it into filter paper, and then let the solvent evaporate. This process was much faster than the solvent-induced decomposition of the clusters. An Au film on Mylar was used as a bulk reference. The ligand contribution was modeled using EXAFS data from samples of sodium chloroaurate and $ClAuP(C_6H_5)_3$, also imbibed into filter paper. All samples had x-ray optical depths of less than 0.1 to avoid self-absorption. The samples were placed in foil packets for loading into the cryostat, so that the samples were isothermal. The cryostat was a Janis closed-cycle model with Mylar windows for the incident, transmitted, and fluorescence x rays. EXAFS detection was by fluorescence, using a plastic scintillator. The EXAFS measurements were done on Beamlines X-15A and X-18B at the National Synchrotron Light Source (NSLS) at the Au L_{III} edge. Absorption edges were measured with an Au reference foil after the sample. Transmission data on this foil were gathered simultaneously with fluorescence data on the samples. This procedure guarded against drifts of the energy scale. The data on Au foil showed detail comparable to that shown in the reference spectra included by EXAFS Materials, Inc. with the ir set of reference foils.

III. EXAFS ANALYSIS

EXAFS data were collected from 100 eV below the edge to 1000 eV above it. Background removal, normali-

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zation, and Fourier filtering were done in the usual way.[8] The background-subtracted data were multiplied by k^1. The zero of energy was taken to be the position of the first inflection point of the edge. To model the ligand shell, we used the Au-Cl signal from sodium chloroaurate. The error incurred in representing the phosphorus ligands as Cl is small. Since the distance obtained for the samples were close to those of the models, the curved-wave corrections[9] could be assumed to cancel and hence were ignored.

To extract mean-square relative displacements (MSRD's; defined as the second moment of the distance distribution as seen by EXAFS), we used a new procedure in the analysis of the filtered signals. We assumed that the signal from the cluster at a given temperature consists of an Au-Au signal and an Au-Cl signal. Instead of fitting the filtered data for each temperature separately, we fit them all together, assuming common values for the distances, coordination numbers, and energy origin shifts for Au-Au and Au-Cl, and individual values for the MSRD's at each temperature. Thus, for a set of M filtered signals, each for a given temperature, we have $2M+6$ fitting parameters, while the traditional method of separate fitting requires $8M$ parameters. In our case, we have $M=10$, and so we use 26 parameters instead of 80. Our data are taken over a range of $\Delta k=13$, with a Fourier filter of width 1.89 Å. By the formula of Lee *et al.*,[8] there are 15.3 independent data in each filtered signal. Consequently, 153 data are fitted with 26 parameters, an improvement over the 80 needed when fitting separately. This procedure is statistically sounder than most common MSRD analysis methods, because unlike the long-ratio technique, it does not overweight the high-k points. Also, no one temperature is singled out for special treatment as the model.

We searched for a possible asymmetry in the radial distribution by extending the above fitting procedure. Instead of a Gaussian, we assumed that the Au shell is described by a Gaussian-broadened exponential tail function. The width of this tail is a measure of the asymmetry of the distribution, and was assumed to be temperature independent. When we added this extra parameter, the fit did not improve noticeably. Thus, while we can not rule out a small asymmetry, we can say that the data are consistent with a symmetric distribution.

The bulk MSRD's were extracted by a slightly different procedure. The above fitting method requires that there be a known model. Since the bulk is its own model, we would have to set aside one temperature as a reference for use in the fit. Instead, we used a variation on the consensus amplitude[10] method. We assume that the signal for the ith k value in the jth temperature is given by

$$\chi_{ij}=\chi_i^0\exp(-2\sigma_j^3k_i^2) \quad (1)$$

and fit this expression to the data. The fit parameters are the χ_i^0 and the σ_i, with the constraint that $\sigma_1\equiv 0$. Again, this method does not overemphasize low-amplitude data at high k, and does not single out any one temperature as being different, except that one must choose a reference for σ_j. This is done by requiring that the lowest temperature be considered $\sigma=0$. Our method was compared to the consensus amplitude method, and to the above group least-squares fitting, using the 8-K data as a reference. The results were very similar in all cases.

It has been found[11] that EXAFS MSRD's are empirically linear in $T^{1.5}$. This relation also holds for x-ray diffraction Debye-Waller factors.[12] This form is obeyed in our data so we can express our result in terms of the static MSRD (the intercept in a σ^2-$T^{1.5}$ plot) and the "vibration factor" (VF). The VF is the slope of the best-fit line in such a plot. The error bars can be judged by the scatter in this plot to be $[\pm 2(4)]\times 10^{-4}$ Å^2 for the bulk (cluster).

IV. ELECTRONIC PROPERTIES

The optical-absorption spectrum of the cluster is shown in Fig. 1. The overall decrease of absorbance with wavelength resembles that of suspensions of fine metal particles. The shoulder at 520 nm is close to the plasmon peak for bulk gold or gold colloids. This sort of bump has been seen in a number of metal-cluster systems,[4] and is thought to be a plasmon feature. This interpretation supports the notion of the Schmid cluster as having metallic properties.

In Fig. 2 we show the x-ray-absorption edge for the cluster, compared with that for bulk gold. We see that the cluster has all the features of the bulk, but attenuated and broadened. The main edge is at the same position as in the bulk, suggesting that the formal charge on the Au atoms is zero, as in the metal. That the same general features are observed for cluster and bulk supports the idea of the cluster as a small piece of bulk. The small size of the cluster makes multiple scattering less probable than in the bulk, and so near-edge x-ray-absorption fine-structure (NEXAFS) –type features could be expected to be attenuated, as observed. Similar edge spectra have been obtained for Au particles evaporated onto Mylar, and explained with similar reasoning to that above.[13]

From the optical and x-ray absorption, we see that the cluster can better be understood as a small chunk of bulk than as a molecule. Thus, since it has been shown that the optical[14] spectra for 13-atom clusters and the x-ray photoemission spectroscopy (XPS) spectra[15] for 11-atom clusters are very different from those in the bulk, we can argue that metallic collective behavior starts somewhere between 13 and 55 atoms.

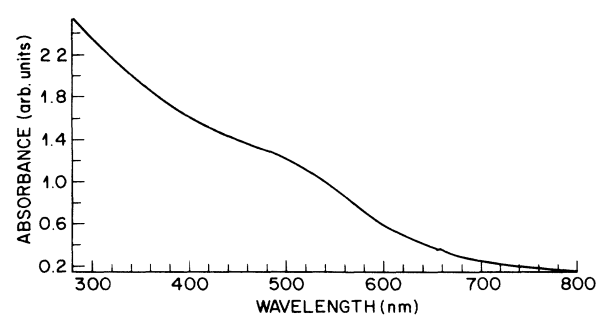

FIG. 1. Optical absorption for a THF solution of the gold cluster.

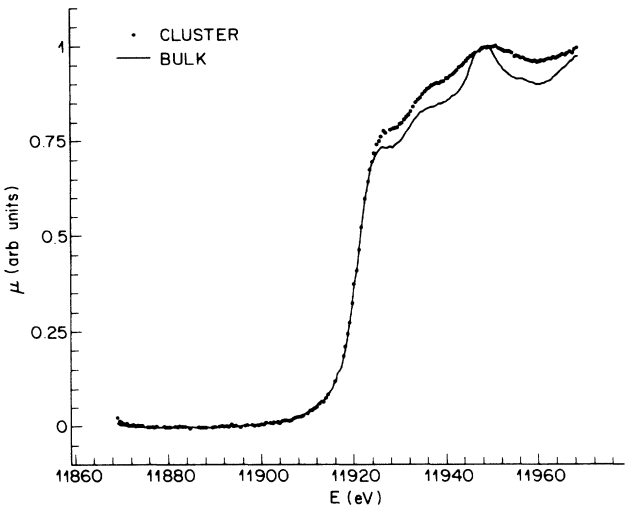

FIG. 2. X-ray absorption edges for Au in cluster (dotted line) and bulk (solid line) forms. The edges are normalized for equal height at the peak.

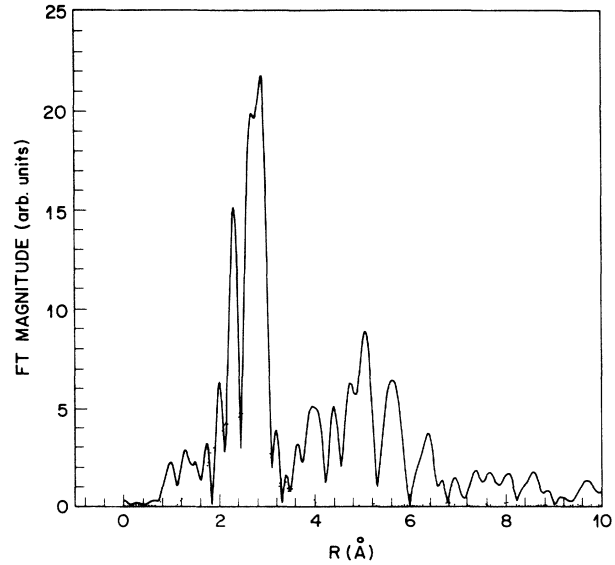

FIG. 4. Fourier-transform (FT) magnitudes for bulk Au (solid line) and the cluster (dotted line) at 8 K. The peaks are split because of the dips in amplitude vs k characteristic of electron scattering from heavy atoms.

V. STRUCTURE

Figure 3 shows an EXAFS spectrum taken at 8 K for the cluster compared with one of bulk Au at the same temperature, and Fig. 4 shows the Fourier magnitudes corresponding to Fig. 3. We see tha the amplitude of the cluster spectrum is lower than that of the bulk, and that the oscillations are quite sinusoidal, as would be seen if there were only first nearest neighbors visible. Analysis bears out these simple conclusions. The coordination number extracted from a two-shell (Au-Au+Au-ligand) fit as explained above is 7.8 ± 1, which compares well with the expected value of 7.85. The higher neighbors are not clearly visible in the Fourier transform. After dividing the complex signal by the complex amplitude for pure Au and retransforming, a procedure known to sharpen Fourier peaks in EXAFS spectra, a broad feature emerges near the second-neighbor position. However, the back-transform of this feature does not yield to analysis, suggesting that this shell is highly disordered. In addition, a ligand shell is seen, which is modeled as an Au-Cl shell at 2.31 ± 0.1 Å distance and 0.2 coordination number. This coordination number is uncertain by a factor of 2, due to the nonorthogonality in the fit of the coordination number and the MSRD for the minor shell. However, the value quoted is reasonable for a ligand shell surrounding a cluster of the Schmid structure.

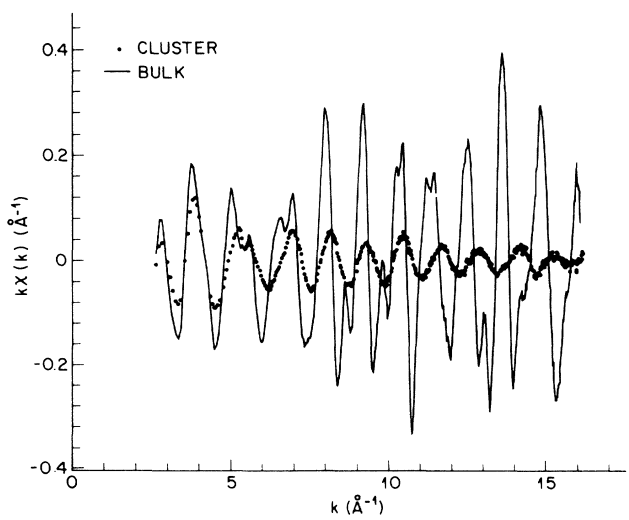

FIG. 3. k^1-multiplied EXAFS spectra, $k\chi(k)$, for bulk Au (solid line) and the cluster (dotted line) at 8 K.

The Au-Au distance is 2.803 ± 0.01 Å, which is distinctly smaller than the bulk distance of 2.878 Å. This difference can be explained as an effect of the Gibbs pressure, and is comparable to what other workers have seen in clusters.[16] There is also a static strain of mean-square value 0.0057 Å^2, which shows that the cluster is not a perfect cuboctahedron, but is slightly distorted, perhaps due to an anisotropy in the surface stress. This distortion may explain why the higher shells are not seen.

In the above we have tacitly assumed that the cluster is the Schmid cuboctahedron, rather than the Mackay icosahedron, which would also have 54 or 55 atoms. While we have no direct experimental evidence that the cluster is cubic, we can make some plausibility arguments from previous data by Schmid *et al.* The stoichiometry is such that there must be about 12 triphenylphosphine and 6 Cl ligands on each cluster. On an icosahedron, it is easy to find 12 symmetry-equivalent positions for ligands, but there is no way of placing six Cl atoms without losing the icoshadral symmetry. The most symmetric placements of Cl atoms would cause a cubic distortion. The obvious places for the triphenylphosphine groups are the vertices. Placing them there leaves 20 uncovered sites,

which are threefold hollows centered on the faces. There is no clear reason why Cl should only attach to 6 of 20 otherwise equivalent sites, nor why it should take a threefold hollow position, which is not often seen in the cluster chemistry of this ligand. By contrast, the Schmid model provides symmetry-equivalent sites for 12 triphenylphosphine ligands and for six Cl ligands in a natural way. Thus, we can say that the cluster is probably cuboctahedral, although more work needs to be done in order to rule out the icosahedral models. We will assume the cubactahedral structure in what follows.

We conclude that the structure and electronic properties of this cluster are as expected for a liganded chunk of fcc gold.

VI. VIBRATIONS

Now we come to the thermal vibrations. The MSRD's for the bulk and the cluster, relative to bulk Au at 8 K, are plotted in Fig. 5. To make the slopes more visible, an offset of 5×10^{-3} Å^2 is subtracted from the values for the cluster. We see that the MSRD's for both cluster and bulk show excellent fits to the $T^{1.5}$ law, with coefficients of 0.88×10^{-6} Å^2 K$^{-1.5}$ and 1.27×10^{-6} Å^2 K$^{-1.5}$, respectively. Thus, the cluster's vibration factor is 43% less than that of the bulk. This is in contradiction to some other results on evaporated cluster,[5,17] in which the cluster is found to vibrate more than the bulk. How the clusters can be stiffer than the bulk is the subject of the following theory.

We consider two effects of size on vibration. First, the cluster is under surface pressure, which leads to a volume contraction and thus an increase in all the elastic moduli over those in the bulk. The equation of state for Au has been carefully researched by Anderson *et al.*[18] Our distance measurement shows a volume contraction of about 7.6%, which then leads to an increase of the bulk modulus by 63%. Since both the bulk modulus and the EXAFS DWF have to do with changes in the interatomic distance, it makes sense to use the bulk modulus instead of either shear modulus to compute the effect of pressure on the DWF. The volume contraction is equivalent to a pressure of 12 GPa. Note that the modulus is nonlinear in the volume, so a simple estimation involving the Gruneisen constant will lead to an underestimate of the stiffening. We thus see that the Laplace contraction creates a stiffening of the cluster.

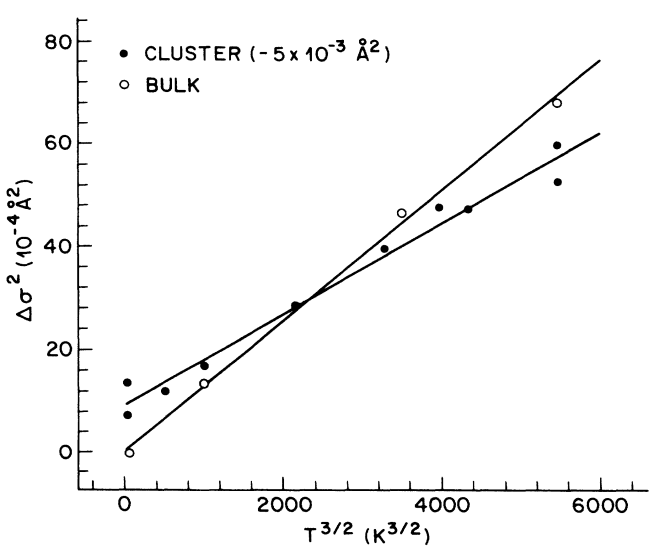

FIG. 5. Plot of $\Delta\sigma^2$ vs $T^{1.5}$ for cluster (open circles) and Au bulk (solid circles) samples. $\Delta\sigma^2$ is referenced to bulk Au at low temperatures. An offset of 50×10^{-4} Å^2 has been subtracted from the cluster values.

Offsetting the contraction effect is the effect of surfaces. Surface modes occur at lower frequencies than those of the bulk, so contribute to an increased vibrational amplitude. To estimate this effect, we did a simple first-neighbor, central-force calculation of the modes of cuboctahedral clusters containing 13, 55, and 177 atoms. These shapes are generated by starting with an atom at (000) and adding fcc neighbors up to ($hh0$), with $h=1,2,3$. The Schmid cluster is thought to be the $h=2$ member of the series. The high-temperature behavior of the DWF is parametrized by the -1 moment of the frequency distribution, weighted by an EXAFS polarization factor. This polarization factor represents the contribution of each mode to the mean-square fluctuation in distance between nearest-neighbor atoms. This number should be proportional to the VF of a hypothetical springs-and-masses cluster. To find the value for the bulk, we plotted the moment values against $N^{-1/3}$, with N the number of atoms in the cluster. This abscissa is equivalent to an inverse diameter, for large clusters. On such a plot, the points for the cuboctohdra fall on a line, which can be extrapolated with some confidence to $N^{-1/3}\rightarrow0$, or the bulk case. We find from this procedure that the 55-atom model cluster has a VF which is 1.17 times that of the model bulk. Previous calculations come up with 1.22–1.25 as factors,[5,17] but these do not include the EXAFS polarization weighting. We assume then that the model cluster represents the effect of surface modes in the real system. Thus, to predict the DWF for the real cluster relative to the real bulk, we divide the surface-mode enhancement factor (1.17) by the relative bulk modulus for the cluster (1.63), and find that the bulk is predicted to vibrate 1.35 times as much as the cluster, as compared to the found 1.43 ratio.

VII. DISCUSSION

Our data show the cluster to be metallic-like from optical and x-ray-absorption viewpoints, with a structure consistent with the cuboctahedral Schmid model. The interatomic spacing is contracted, presumably because of Gibbs pressure, and there is static distortion. The gross vibrational properties of this cluster can be quantitatively understood in terms of a combination of surface-induced compression and softening due to surface modes. We have thus established that the Schmid cluster is a model case in which a bulk description, suitably modified, describes a small cluster.

The stiffening of the cluster relative to the bulk is

surprising, yet seems predictable from known effects. One might then ask if this effect is special to Au or may be observed in other clusters. To observe this effect, one needs a cluster which is enough like the bulk so as to be comparable with it. This implies that the ligands should be as chemically unobtrusive as possible. The ratio of the bulk modulus to the surface tension must be high enough to yield a significant contraction. This suggests that "soft" metals such as Ag, Pb, etc. are good candidates. By this theory, one might predict that the effect would be hard to observe in Pt or Rh, which are much stiffer than Au. Studies of comparable clusters should prove interesting.

Note added. While the present paper was undergoing referee review, another group[19] published similar work to ours, with results consistent with the present ones. However, their measurements were done only at room temperature, so that they could not explore the vibrational effects which we see; also, they did not include ligand shells in their fits, and their data were noisier than ours.

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