

Evidence for High T_C Superconducting Transitions in Isolated Al_{45}^- and Al_{47}^- Nanoclusters

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Abstract Heat capacities measured for Al_{45}^- and Al_{47}^- nanoclusters have reproducible jumps at ~ 200 K. These jumps are consistent with theoretical predictions that some clusters with highly degenerate electronic states near the Fermi level will undergo a transition into a high T_C superconducting state. An analysis based on a theoretical treatment of pairing in Al_{45}^- and Al_{47}^- agrees well with the experimental data in both the value of the critical temperature and in the size and width of the jumps in the heat capacity.

Keywords Nanoclusters · Peaks in the heat capacity · Pairing transition

Superconductivity, the flow of electric current without resistance, occurs in a wide variety of materials when the temperature drops below a critical temperature, T_C . The transition to the superconducting state is accompanied by diamagnetism and by a jump in the heat capacity. The superconducting transitions observed to date are all below 135 K under atmospheric pressure and below 168 K under high pressure, and they are mostly associated with bulk systems [1–3]. Recently, Kresin and Ovchinnikov proposed that

a superconducting transition can occur for some metal nanoclusters with 10^2 – 10^3 valence electrons [4–6]. The transitions are expected to occur near electronic shell closings. It is well established that the electronic energy levels in metal clusters are not evenly spaced, but instead adopt a shell structure similar to that found in atoms or nuclei [7–11]. The highest energy occupied electronic energy levels become highly degenerate at spherical shell closings (“magic” numbers) while between shell closings Jahn–Teller distortions lift the degeneracy. Under special circumstances, which we describe below, the shell structure is expected to strengthen pairing correlations, and leads to elevated values for the critical temperature for a transition to the superconducting state. The superconducting state of small nanoclusters is directly related to the phenomenon of pair correlation. For bulk superconductors, it leads to an appearance of the dissipationless state. For the clusters of interest, the manifestation is different and is similar to that in atomic nuclei: The pairing leads to a strong modification of the energy spectrum.

In this work, we report heat capacity measurements for isolated, single-sized aluminum nanoclusters. The heat capacity measurements were performed for a number of aluminum nanoclusters, and both Al_{45}^- and Al_{47}^- were found to display a clear, reproducible jump in their heat capacities at around 200 K. As we show below, this behavior is consistent with theoretical predictions for a superconducting transition in aluminum nanoclusters [4–6]. A transition temperature of 200 K exceeds those found in bulk systems. While it is difficult to imagine direct applications for superconductivity in isolated nanoclusters, these results suggest the feasibility of generating superconducting nanowires by aligning nanoclusters on a surface or in a nanotube. The nature of the nanocluster (i.e., number of atoms and perhaps even the composition) could then be adjusted to optimize the electronic structure for high T_C superconductivity. The specific

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alignment of size-selected nanoclusters on a surface or in a nanotube is beyond our current capabilities; however, the technological hurdles are not insurmountable.

The heat capacities were measured using a novel multicollision induced dissociation method where the dissociation threshold is determined as a function of the cluster's initial temperature [12–15]. As the temperature is raised, the dissociation threshold decreases due to the increase in the cluster's internal energy. The change in the dissociation threshold with temperature provides a measure of the heat capacity. The apparatus used to measure the heat capacities has been described in detail elsewhere [12–15]. Briefly, aluminum cluster anions are generated by pulsed laser vaporization of a liquid aluminum target [16]. Once formed, the cluster ions travel into a temperature variable extension where their temperature is set. Upon exiting the extension, the cluster ions are focused into a quadrupole mass spectrometer where a particular cluster size is selected. The size-selected clusters are then focused into a high pressure collision cell, where they are heated by collisions with the He buffer gas and may dissociate. The undissociated parent ions and the fragment ions are subsequently analyzed by a second quadrupole mass spectrometer. The fraction of the cluster ions that dissociate is determined from the mass spectrum as a function of the ion's translational energy, and the translational energy required for 50% of the cluster ions to dissociate (TE50%D) is determined from a linear regression. The derivative of TE50%D with respect to temperature is proportional to the heat capacity. The proportionality constant is related to the fraction of the ion's translational energy that is converted into internal energy as the ion enters the collision cell. This fraction is estimated from a modified impulsive collision model [17–19]. Figure 1 shows plots of heat capacities determined for aluminum cluster anions with 43–48 atoms for temperatures below room temperature. The heat capacities are plotted relative to the classical value $(3n - 6 + 3/2)k_B$, where n is the number of atoms in the cluster. The thin dashed lines in the figure show heat capacities derived from a modified Debye model that takes into account the finite size of the cluster [20]. There are peaks in the heat capacities for all of the clusters at temperatures substantially above 300 K. These peaks which are due to melting transitions, and in some cases, premelting transitions are discussed in more detail elsewhere [21]. In the heat capacities recorded below 300 K (see Fig. 1), there are reproducible jumps at around 200 K for both Al_{45}^- and Al_{47}^- . These jumps are not due to melting or premelting transitions because they occur at too low a temperature. It is unlikely that they are due to structural transitions for the same reason. The structural transitions we have observed with aluminum clusters lead to dips rather than peaks in the heat capacities, and they occur at temperatures significantly above room temperature [13].

As noted above and demonstrated below, we believe that the observed jumps in heat capacity at 200 K for Al_{45}^- and

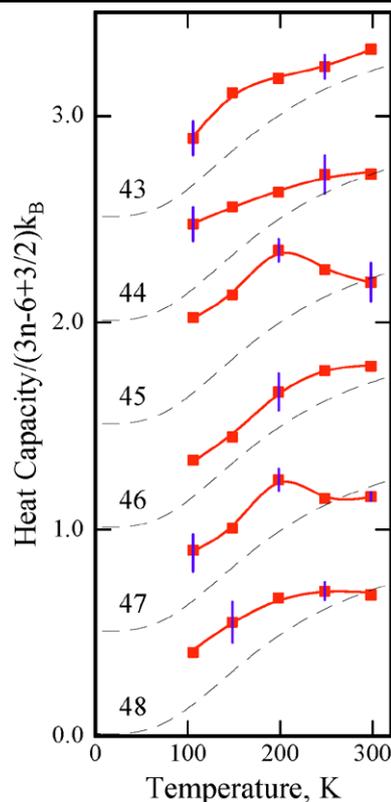


Fig. 1 (Color online) Heat capacities for the size-selected, aluminum nanoclusters with 43–48 atoms recorded below 300 K. The points are the results of multiple independent measurements, and the vertical bars show uncertainties (\pm one standard deviation). The heat capacities are plotted relative to the classical value $(3n - 6 + 3/2)k_B$, where n is the number of atoms in the cluster. The thin dashed lines show heat capacities derived from a modified Debye model that takes into account the finite size of the cluster. The obvious jumps observed at around 200 K in the heat capacity for Al_{45}^- and Al_{47}^- nanoclusters are believed to be due to the superconducting transition

Al_{47}^- correspond to the transition into a superconducting state. A superconducting transition has been observed at low temperature for large nanoparticles ($N \gtrsim 10^4$, N is the number of delocalized electrons) [22–25] and a nascent superconducting state has been invoked to explain some unexpected observations for small niobium clusters [26].

Al clusters are of special interest because they display an electronic shell structure [27–29]. It has been suggested that the presence of an electronic shell structure can have a dramatic impact on electron pairing [30], and especially [31]. Note that atomic nuclei (see [32, 33]), nanoparticles and granular metals (see, e.g., [34, 35]) are the examples of finite systems; one can observe various manifestations of the superconducting state (Cooper pairing) in these systems. For nanoclusters, one can observe the odd-even effect in their spectra, diamagnetism, jump in heat capacity, Josephson tunneling for the cluster network, etc.

According to [4–6], for clusters with parameters satisfying special but realistic conditions, one can expect a

great strengthening of the pairing correlation and, correspondingly, a large increase in the critical temperature [4–6]. These conditions are: the proximity of the electronic state to a complete shell (“magic” number) and a relatively small gap between the highest occupied shell (HOS) and the lowest unoccupied shell (LUS). Al_{45}^- and Al_{47}^- both satisfy these criteria. The electronic shell structure for aluminum clusters as well as for gallium clusters (gallium and aluminum atoms have a similar electronic structure) has been observed experimentally [27–29]. According to photo ionization data [27–29], both Al_{45}^- and Al_{47}^- are close to a shell closing. A high T_C is caused by large values of orbital momenta l and corresponding large shell degeneracy [4–6]. That is why the situation is most favorable for relatively large clusters with $N \gtrsim 10^2$. According to theoretical predictions, the values of T_C observed in the present paper are realistic. Indeed, consider, for example, the cluster Al_{45}^- . This cluster contains an even number of electrons (this is essential for the pair correlation) and it is close to the shell closing with $N = 138$ [7–11, 27–29]. The equation for the pairing order parameter $\Delta(\omega_n)$ has the following form [4–6]:

$$\Delta(\omega_n)Z = \eta \frac{T}{2V} \sum_{\omega_n'} \sum_s D(\omega_n - \omega_n') F_s^+(\omega_n') \quad (1)$$

Here

$$D(\omega_n - \omega_n', \tilde{\Omega}) = \tilde{\Omega}^2 [(\omega_n - \omega_n')^2 + \tilde{\Omega}^2]^{-1} \quad (1')$$

$$F_s^+(\omega_n') = \Delta(\omega_n') [\omega_{v'}^2 + \xi_s^2 + \Delta^2(\omega_n')]^{-1}$$

are the vibrational propagator and the Gor’kov pairing function (see, e.g., [36]), respectively, $\omega_n = (2n + 1)\pi T$; $n = 0, \pm 1, \pm 2, \dots$, $\xi_s = E_s - \mu$ is the energy of the s ’th electronic state referred to the chemical potential μ , V is the cluster volume, $\eta = \langle I \rangle^2 / M \tilde{\Omega}^2$ is the Hopfield parameter, $\langle I \rangle$ is the electron-ion matrix element averaged over electronic states involved in the pairing, M is the ionic mass, and Z is the renormalization function. Equation (1) looks similar to that in the theory of strong coupling superconductivity (see, e.g., [37–39]), but is different in two key aspects. First, it contains a summation over discrete energy levels E_s and, in addition, the position of the chemical potential is determined by the values of N and T . Note that in a weak coupling case ($\eta/V \ll 1$ and correspondingly $\pi T_C \ll \tilde{\Omega}$), one should put in (1) $Z = 1$, $D = 1$, recovering the usual BCS scheme (see, e.g., [38, 39]). For a “magic” cluster, T_C can be calculated from (1) which at $T = T_C$ can be reduced to the following matrix equation (see [4–6]):

$$\det|1 - K_{nn'}| = 0 \quad (2)$$

where

$$K_{nn'} = g \tau_C \sum_j G_j \{ [1 + (n - n')^2 \tau_C^2]^{-1} - \delta_{nn'} Z_n \} \times [(n' + 0.5)^2 \tau_C^2 + \tilde{\xi}_j^2]^{-1} \quad (2')$$

Here $\tau_C = 2\pi T_C / \tilde{\Omega}$, $G_j = 2(2l_j + 1)$, $g = \lambda_b (6\pi \tilde{E}_F / N)$, $\tilde{E}_F = E_F \tilde{\Omega}^{-1}$, $\Delta \tilde{E} = \Delta E \tilde{\Omega}^{-1}$, $\tilde{\xi}_j = \xi_j \tilde{\Omega}^{-1}$, $j \equiv \{H, L\}$, $H \equiv$ HOS, $L =$ LUS, $\tilde{\Omega}$ is the characteristic vibrational frequency of the cluster, $\tilde{\Omega} \approx \Omega_D$, l is the orbital quantum number, E_F is the Fermi energy, and Z_n is the renormalization function. The matrix (2) converges rapidly for $\tau_C > 1$.

For Al_{45}^- clusters, $I_{HOS} = 1$ and $I_{LUS} = 7$, so that $G_H + G_L = 36$. According to measurements, $\Delta E \approx 40$ meV [25]. Substituting the parameters $N = 136$, $E_F \approx 1.3 \times 10^5$ K, $\tilde{\Omega} \approx 350$ K and $\lambda_b \approx 0.4$ [4–6] into (1) and (2), we obtain $T_C \approx 170$ K. A jump in the heat capacities was experimentally observed at temperatures close to this value (see Fig. 1). Note that high value of T_C leads the coherence length being short, similarly to the high T_C cuprates.

One can also evaluate the size of the jump in heat capacity. Let us start with the Ginzburg–Landau expression for the thermodynamic potential Θ_s in the superconducting state near T_C :

$$\Theta_s = \Theta_n - a \tau_C^2 (1 - t)^2 \quad (3)$$

Here, Θ_n is the thermodynamic potential in the normal state, $t = T/T_C$, and a is the material dependent constant introduced in [4–6] and determined by the relation:

$$a = \tau_C^2 \tilde{S} / \pi (\partial \tau_C / \partial g) C \quad (4)$$

where

$$\tilde{S} = 0.5 \sum_{\substack{s, s' \\ n, n' \geq 0}} (f_{n; n+1}^+ + f_{n, n'}^-) \chi_{n; \zeta_s} \chi_{n'; \zeta_s'} \phi_n \phi_{n'} \quad (5)$$

$$f_{n; r}^\pm = [1 + (n \pm r)^2 \tau_C^2]^{-1} \quad (6)$$

$$\chi_{n; v} = [(n + 0.5)^2 \tau_C^2 + v^2]^{-1}$$

C determines the energy gap near T_C , g is the electron-vibrational coupling constant, and ϕ_n is the order parameter. A detailed calculation of the parameter a for the Al_{45}^- cluster will be described elsewhere. However, for many clusters, its value is of order of $a = [3 - 5] \times 10^3$ K. With use of (4) through (6), one can obtain the following expression for the jump in heat capacity:

$$\beta \equiv (C_s - C_n) / 3n = (4\pi^2 / 3) (a / T_C) (T_C / \tilde{\Omega})^2 n^{-1} \quad (7)$$

We normalized the jump to its classical value $3n$ (we set $k_B = 1$). Substituting into (7) the values of a , T_C , n , and $\tilde{\Omega} \approx 30$ meV, we obtain $\beta \approx 0.3 \sim 0.5$ for the clusters of interest,

in good agreement with the jumps found experimentally (see Fig. 1).

The observed jumps are rather broad. The breadth of the transition is caused by thermodynamic fluctuations. This question has been considered previously [4–6]. The thermodynamic fluctuations lead to

$$(\delta T_C/T_C) \approx (\tilde{\Omega}^2/\pi^2 a T_C)^2 \quad (8)$$

Substituting the values for the parameters from above into this expression, we obtain $(\delta T_C/T_C) \approx 10 \sim 15\%$, that is, $\delta T_C \approx 30$ K. This width corresponds quite well to the breadth of the transition observed for the Al_{45}^- and Al_{47}^- clusters. Therefore, the jumps observed in heat capacity for size selected aluminum clusters are entirely consistent with a high T_C superconducting pairing transition predicted by theory [4–6].

In summary, heat capacities measured for size-selected Al_{45}^- and Al_{47}^- show jumps at around 200 K. The jump in the heat capacity is the signature of a phase transition. The features of the phase transition, i.e., the transition temperature, the size and the width of the peak in the heat capacity are all entirely consistent with a recent theoretical treatment of a superconducting transition for metal nanoclusters. This is the first experimental observation of such a transition.

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