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Low-temperature specific heat of Pd nanocrystals

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It is the first time that the quantum electronic effects in metal particles is directly observed in low-temperature specific heat. In 32 Å Pd nanocrystals at T< 1 K the linear coefficient of heat capacity γ deviates from that of the bulk Pd and reduces to a lower value. This is as expected to the case if measuring temperature T << the energy level spacing δ. At lower temperatures a quadratic temperature dependence of electronic specific heat is recognized, indicating that the energy level distribution in Pd metal is an orthogonal function;one of the cases presented by Kubo theory.

1. INTRODUCTION

The electronic quantum effects in metal particles have been widely studied by all possible means for last two decades, although a few of phenomena connecting to these effects have been observed in some experiments, for example magnetic susceptibility. There are no experiments on heat capacity that show clear evidence of the quantum size effect. Since the spacing of electron energy levels is inversely proportional to the cubic of particle radius d, if the size of metal particles can be well controlled and the experimental temperature is lower enough as compared to the electronic energy-level spacing δ, then the electronic specific heat of a metal particle would not be a linear temperature dependence but should show an exponential dependence. In this paper we report the result of heat capacity measurements on 32-Å and 48-Å Pd nanocrystals for 0.3K< T < 25K. The expected average electronic energy-level spacings for 32-Å and 48-Å Pd nanocrystals are 5.3K and 1.5K respectively [1], thus we have very good opportunity to see the quantum electronic size effect at temperatures around 0.5K..

2. EXPERIMENTAL DETAILS

Three specimens, one bulk Pd and two Pd nanocrystals with average sizes about 48 Å and 32 Å, have been prepared with a similar method to that of 84-Å Pd nanocrystals reported early [2]. In Fig. 1 the distribution of particle sizes for 32-Å Pd nanocrystals obtained by transmission electron microscopy is shown. The measurements of low-temperature specific-heat were performed using a thermal-relaxation

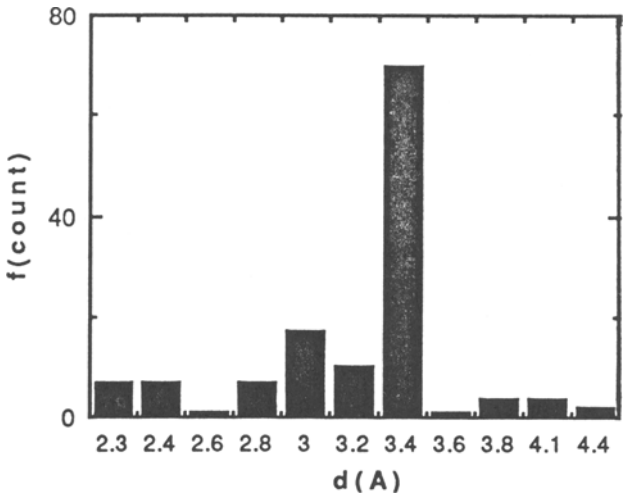

FIG. 1. The distribution of particle sizes for 32-Å Pd nanocrystals observed by transmission electron microscopy.

microcalorimeter, one had been described in reference [2].

3. RESULTS AND ANALYSIS

The result for the specific heat of bulk Pd and 48-Å and 32-Å Pd nanocrystals is shown in Fig. 2 and Fig. 3. The specific heat of bulk Pd is fit by Eq. (1) with γ = 9.7mJ/K² mol Pd and $\beta = 9.5\times10^{-2}$ mJ/K⁴ mol Pd. The

$$C(T) = \gamma T + \beta T^3 \quad (1)$$

enhanced specific heats of phonons are shown in Fig. 2 and are fit by Eq. (2) provided by Baltes and Hilf with the sound velocities 1200m/s and 1130m/s for 48-Å and 32-Å Pd nanocrystals respectively.

$$C_p = \sum_l \sum_s \frac{V_m\ (2l+1)\ K_B\ z^2\ e^z}{4\ R^3\ (e^z-1)^2} \quad (2)$$

with

$$z = \frac{\hbar c\, a'_{l,s}}{K_B\ R\ T}$$

The maximum l_{max} satisfies the condition $\sum_1^{l_{max}}(2l+1) \le N$, where N is the number of atoms contained in a particle, R is the particle radius, V_m is the mole volume and $a'_{l,s}$ is the sth zero of the derivative of the lth spherical Bessel function, and c is the velocity of transverse phonons. In Fig. 2 an anomaly bump observed at temperature around 6K might be due to Pd oxidation, such as PdO. No any unusual phenomena was observed for 48-Å Pd nanocrystals at temperatures < 1K, whereas a reduction of specific heat at T < 1 K was observed in 32-Å Pd nanocrystals. The specific heat of 32-Å Pd nanocrystals after phonon subtraction is shown in the inset of Fig. 3 for T < 1K. The linear temperature dependence of C/T shows the low-temperature specific heat has quadratic temperature behavior, it is one of the cases presented by Kubo and his colleagues [4],i.e., the energy level distribution in Pd metal is an orthogonal function.

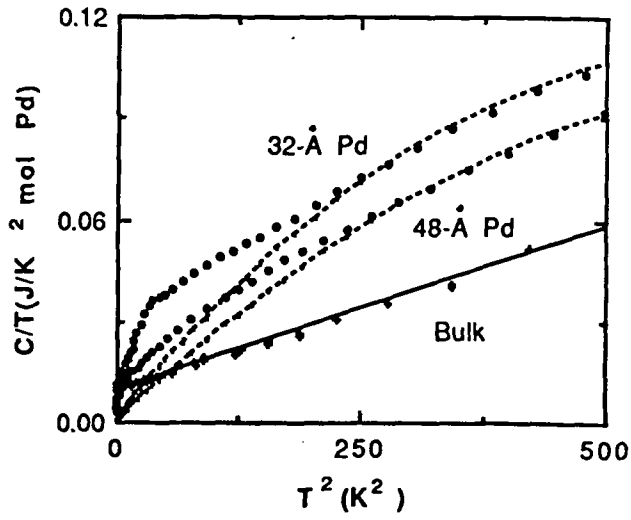

FIG. 2. C/T vs T² for 48-Å and 32-Å Pd nanocrystals. The crosses represent Bulk Pd, the empty circles represent 32-Å Pd nanocrystals, the solid circles represent 48-Å Pd nanocrystals and the dash lines are the lattice phonons fits (see text).

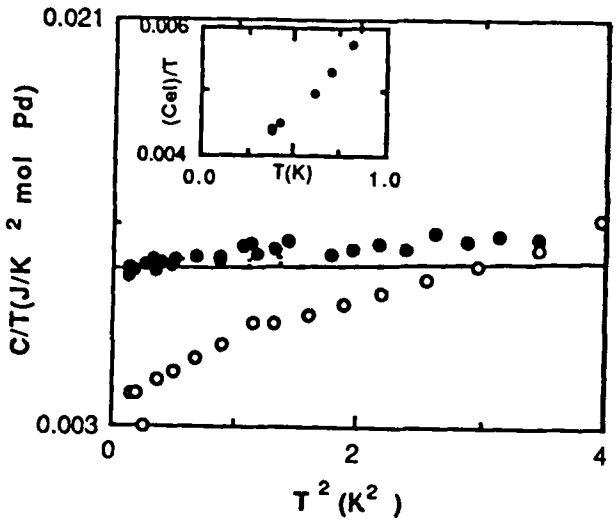

FIG. 3. The specific heat of 32-Å and 48-ÅPd nanocrystals for T < 3K. Inset: specific heats after phonon subtraction for T < 1K.

CONCLUSIONS

A direct observation of electronic quantum size effect is shown in the specific heat in 32-Å Pd nanocrystals and the electronic energy level distribution is qualitatively recognized as an orthogonal function for the Pd metal.

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