# Size Dependence of Critical Transition Temperature of MgB$_2$

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We have studied the effect of crystal size $D$ on the critical transition temperature $T_c(D)$ of MgB$_2$ physically divided into the individual particles on the nanometre scale. It is found that $T_c(D)$ decreases with the decreasing of $D$. A thermodynamic model for $T_c(D)$ was established quantitatively based on the size dependence of the cohesive energy. An agreement between the model prediction and the experimental results was found.

## 1.    Introduction

The discovery of a superconducting transition at 39 K in MgB$_2$ initiated enormous interest both to understand the phenomenon and to exploit its remarkable intrinsic performance for magnetic and electronic applications [1,2]. In recent years size effects on the critical transition temperature $T_c(D)$ of MgB$_2$ nanocrystals have been extensively investigated theoretically and experimentally with $D$ denoting the crystal size [3-5]. When $D$ of low-dimensional materials decreases to the nanoscale, electronic, magnetic, optic, catalytic and thermodynamic properties of the materials are significantly changed, having a substantial difference from their bulk counterparts [6]. Understanding the physical nature behind the new properties is desired for fabricating the materials for practical applications [6].

In experiments, it was found that $T_c(D)$ of the MgB$_2$ nanocrystals progressively reduce with $D$ decreasing [3,4]. In our work, it has been reported that MgB$_2$ nanocrystals were fabricated by the physical reduction method [7]. Commercial bulk MgB$_2$ crystals (99% purity) were milled in tungsten carbide (WC) bowls purged with Ar. The crystal size of MgB$_2$ nanocrystals was determined by X-ray diffraction and verified by high resolution transmission electron microscopy. It is in a range of 2.5 to 64.1 nm (about 10% size deviation). Through measuring the magnetic moments, we find that the $T_c(D)$ decreases with the decreasing of $D$, which is in agreement with other experimental results. However, further theoretical work is still needed to seek the physical nature behind the $T_c$-suppression and a $T_c(D)$ function is highly desirable.

In this contribution, we demonstrate that the cohesive energy, $E$, determines a number of physical-chemical properties of nanocrystalline materials. Based on this understanding, a function to predict $T_c(D)$-suppression of superconductive nanocrystals is established in a form of a model for size-dependent cohesive energy $E(D)$. The accuracy of the developed model is verified with the available experimental data of MgB$_2$ nanocrystals.

## 2.    Methodology

The profile of Lennard-Jones potential is determined by both bond strength, $\varepsilon$, and equilibrium atomic or molecular distance, $h$ [8]. Note that $E$ is the sum of $\varepsilon$ over all the coordinates of the specific atom with coordination $z$, and $E = zN_a\varepsilon/2$ with $N_a$ being the Avogadro constant (Note that only the nearest-neighbor interaction is being considered in the above formula. This is the case for $P622$-symmetried MgB$_2$ due to considerably weak next-nearest-neighbor interaction). Thus, the variation of the potential profile for nanocrystals,

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which is related to the crystallographic structures and the corresponding transition functions, should be determined by the change of both $E$ and $h$. In this case, the size effects on the physical-chemical function could be considered to contribute by the change of $E$ and $h$. As the change of $h$ is usually in the range of 0.1%-2.5% even when $D < 20$ nm [9], the size effect on $h$ can be neglected. Therefore, size dependence of physical-chemical functions could be predicted if the $E(D)$ function is available.

Based on Ising premise, $T_c$ is determined by the spin-spin exchange interaction $E_{exc}(T)$ [10]. The latter is the sum of a portion of the cohesive energy $E$ and the thermal vibration energy $E_v(T)$ where $T$ denotes the temperature [5,10], e.g. $E_{exc}(T) = AE + E_v(T)$ with $A$ ($0 < A < 1$) being a coefficient. Based on the mean field approximation and Einstein′s relation, $E_v(T) = k_B T$ as a first order approximation with $k_B$ denoting the Boltzmann constant [5,10]. At the critical temperature, $E_{exc}(T) \approx 0$ and the thermal vibration energy required for disordering the exchange interaction is a portion of the cohesive energy at $T = 0$ [5,10]. Thus, $T_c \propto E$. It is assumed that $T_c(D)$ has the same size dependence of $E(D)$ since the nature of any phase transition is related with the potentials of the two related phases of the crystals. As a result, $T_c(D)/T_c(\infty) = E(D)/E(\infty)$.

Combining the $E(D)$ function reported in literature [11], and the above considerations, a general correlation can be expressed as,

$$\frac{T_c(D)}{T_{cb}} = \frac{E(D)}{E_b} = \left[1 - \frac{1}{(2D/h) - 1}\right]\exp\left[-\frac{2S_b}{3R}\frac{1}{(2D/h) - 1}\right] \qquad (1)$$

where $S_b$ is the bulk evaporation entropy of crystals, $T_{cb}$ and $E_b$ show bulk critical transition temperature and cohesive energy, respectively, and $R$ denotes the ideal gas constant [11].

## 3. Results and discussion

The modelling result with Eq. (1) is plotted to compare with the experimental results for $T_c(D)/T_{cb}$ of $MgB_2$ nanocrystals in Fig. 1. The solid line denotes the model prediction based on Eq. (1) where $S_b \approx 13R$ as a first order approximation, which is equal to that of the mean value of the most elements, and $h = 0.352$ nm [12]. The symbol ♦ with the error bars denotes our experimental results [7], Δ [3] and ∇ [4] show other experimental results.
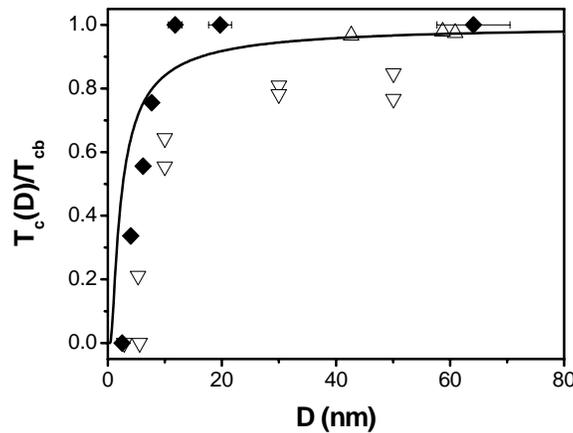


Fig. 1. $T_c(D)/T_{cb}$ function of $MgB_2$ superconductive nanocrystals.

As shown in this figure, $T_c(D)$ decreases with $D$ decreasing. Although there is scatter in the experimental results, our model prediction shows the same trend as the data in a very wide span of size range. This exhibits the accuracy of Eq. (1). Certainly, there is deviation between

them since the Einstein′s relation is not accurately valid in low temperature, which needs further improvement. Note that all parameters have clear physical meaning in the developed model, which makes it easier to reveal the physical nature behind the properties.

As a general rule, $\exp(-x) \approx 1-x$ when $x$ is small enough. In such a case, $D > 10$ nm. With the first order approximation, Eq. (1) can be rewritten as,

$$T_c(D)/T_{cb} \approx 1- [1/2+S_b/(3R)]h/D. \tag{2}$$

Eq. (2) obeys thermodynamic rule of low-dimensional materials, that the alternation of size-dependent quantity is associated with the surface/volume ratio, or $1/D$. This further supports the notion that the discussed physical-chemical properties are most likely affected by the severe bond dangling which is induced by the crystal size reduction in nanoscale. However, as the size of the nanocrystals further decreases, namely below 10 nm, the difference between Eqs. (1) and (2) becomes evident [11].

For the smallest crystals ($D = 2.5$ nm) in our experiments, superconductivity is completely depressed. It is noted that the thermodynamics has a statistic mechanics basis. When $D < 2\sim3$ nm, the particles consist of only several ten to hundred of atoms, the statistic meaning is no longer present. In addition, the crystalline structure becomes unstable due to big bond deficit where a cluster with special structure arises. In this case, the long-range ordering vanishes and the bond structures differ from the corresponding crystals. This is outside the scope of our model description since the developed model is only suitable for crystalline materials based on the consideration of a continuous medium.

It is evident from Eq. (1) that $E(D)$ (negative) increases (the absolute value decreases) with a decrease in size due to the increase of surface/volume ratio, which reflects the instability of nanocrystals in comparison with the corresponding bulk crystals [11]. If this increase for both low temperature phase and high temperature phase is almost the same, the relative energetic increase of the low temperature phase is larger than that of high temperature phase. Together with the consideration of entropy where the entropy of high temperature phase is always larger than that of low temperature phase, depression of the transition temperature between them is present.

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