Correlated variation of melting and Curie temperatures of nickel clusters

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The temperature-dependent study of magnetic properties of Ni_N clusters is presented, which reveals an intriguing relationship between Curie ($T_{C,N}$) and melting ($T_{melt,N}$) temperatures. Interestingly, both exhibit similar variation with cluster size; that is, their values are lower than their corresponding bulk values and approach their respective bulk value asymptotically as the cluster size increases. This similarity is justified using model calculations within the mean-field theory applied separately to the surface and core regions and is further quantified as a linear relationship between $T_{C,N}$ and $T_{melt,N}$ for a large range of cluster sizes.

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Two of the most prominent factors affecting the cluster magnetism are the geometrical features and the temperature of the cluster. On the one hand, the structural dependence of the cluster magnetism has been successfully addressed by various zero-temperature (ZT) model approximations which were able to verify the earlier experimentally measured magnetic moments (MMs) reported for small 3*d*–transition-metal clusters (see, for example, Refs. 1–3 and references therein). The non-ZT simulations for magnetic clusters, on the other hand, mostly address structural phase transitions and, to a lesser extent, the temperature dependence of their magnetic features. Special foci of all these studies are the melting ($T^{cl}_{melt,N}$) and Curie ($T^{cl}_{C,N}$) temperatures of the *N*-atom magnetic cluster as well as their variation with the cluster size.[4–10] While a large number of reports exist for $T^{cl}_{melt,N}$, the experimental works on $T^{cl}_{C,N}$ are very limited.[2,11–13] Interestingly, the theoretical investigations for $T^{cl}_{C,N}$ are mostly performed within the Heisenberg approximation to the cluster Hamiltonian.[14–17] A study of temperature-dependent magnetic behavior and, in particular, the dependence of Curie temperature on cluster size are, therefore, very timely.

In the present work, we focus our attention on the temperature-dependent properties of magnetic transition-metal clusters and, in particular, on Ni clusters for which some experimental data are available for comparison. However, as demonstrated in Figs. 1 and 2, a major feature characterizing either the experimental results or those of the non-ZT simulations is the large range of values that have been reported for both their melting temperatures[4–6,8–10] and their MMs (see Ref. 2 and references therein). This discrepancy may reach up to 100% in the former case and 25% in the latter. Taking into account the limited number of available experimental reports on the temperature dependence of the cluster magnetism,[2,11–13] it is fair to say that our knowledge of the temperature dependence of the magnetic features of a cluster cannot be considered conclusive. These include the temperature dependence of the MMs of the cluster atoms, the Curie $T^{cl}_{C,N}$ and Debye $T^{cl}_{\Theta,N}$ temperatures, as well as their evolution with the cluster size, the existence of magnetic phase transitions, etc. Nevertheless, the existing reports have established some general trends, among which we mention the increase of both $T^{cl}_{melt,N}$ and $T^{cl}_{C,N}$ as the number of the cluster atoms, *N*, increases, tending to their corresponding bulk values, T^{bulk}_{melt} and T^{bulk}_{C}, respectively. In particular, for $T^{cl}_{melt,N}$ derived on the basis of the Lindemann index, it is found to increase proportionally to the surface atoms of the cluster[4,5] (see Fig. 1), i.e.,

$$T^{cl}_{melt,N} = T^{bulk}_{melt} - \alpha N^{-1/3}, \tag{1}$$

where α is a fitting constant. The disagreement in the absolute values of $T^{cl}_{melt,N}$ among different theoretical reports may be attributed to the different descriptions of the interatomic potentials used.[4–6,8–10] No analogous trend was suggested for $T^{cl}_{C,N}$.

In the present work, we, therefore, focus our attention on this important feature, namely, the investigation of the variation of $T^{cl}_{C,N}$ with the cluster size, and justify the limited experimental findings about the dependence of the MM of Ni clusters on temperature and cluster size. The intriguing analogy seen in the dependence of both $T^{cl}_{melt,N}$ and $T^{cl}_{C,N}$ on the cluster size, while asymptotically converging to their bulk values, made us wonder about the existence of a possible correlation between these two temperatures.

In order to proceed with this investigation, we need an approach which is computationally efficient, while at the same time retaining the quantum-mechanical approach to these systems. With this in view, we chose our well tested tight-binding molecular-dynamics approximation (TBMDA) scheme, which has provided MMs for small transition-metal clusters in best agreement with experiment.[2] Although TBMDA may not be as robust (as compared to the Monte Carlo

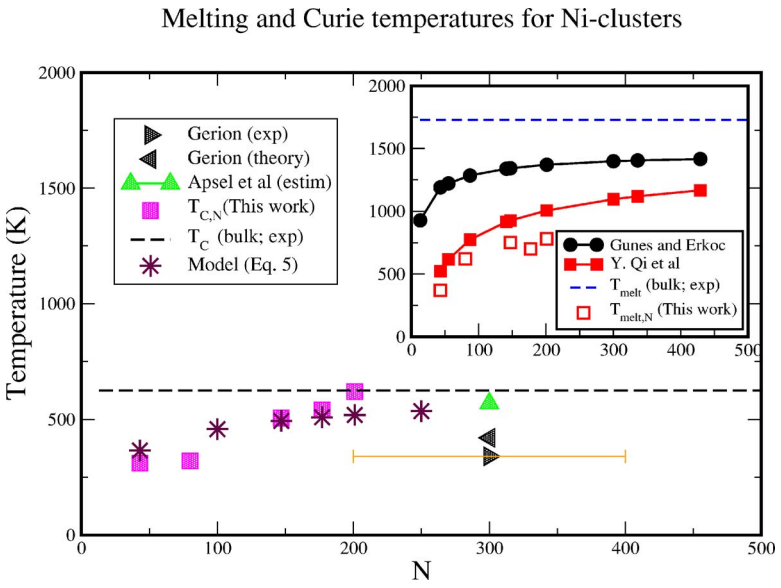

FIG. 1. (Color online) Curie and melting (inset) temperatures for Ni_N clusters. The main graph shows the Curie temperature $T^{cl}_{C,N}$ obtained by various methods. Results of the present work are indicated with filled magenta squares, while the predictions of Eq. (5) are indicated by stars. The experimental values of the Curie temperatures of the bulk Ni are indicated by the black dashed line. The inset shows the melting curves ($T^{cl}_{melt,N}$). The black curve and solid circles show the prediction of Eq. (1) according to Ref. 4; red curve and solid squares are the (interpolated) prediction (obtained using the data of Refs. 5 and 7); open red squares refer to results for $T^{cl}_{melt,N}$ of the present work. The experimental values of the melting temperatures of the bulk Ni are indicated by the blue dashed line.

approach) in sampling the partition functions over the configuration space, its superior computational efficiency makes it preferable for such problems. At the same time, care has been taken to minimize the drawbacks of the TBMDA by choosing initial cluster geometries at or near their universal optimum structures and allowing for a long simulation time.[18]

Due to the presence of *d* electrons, an extensive search of the configuration space at various temperatures using a fully quantum-mechanical approach is computationally prohibitive. In order to make this problem tractable, we combine the classical potential approximation (CPOA) and the quantum TBMDA in a suitable way. The CPOA enables us to relax the geometry of the clusters at their thermodynamic equilibrium at reasonable computational expense while performing molecular-dynamics (MD) simulations. The TBMDA is used to obtain the magnetic features of the clusters within a theory founded on a firm quantum-mechanical footing. That is, our TBMDA is formulated by employing a complete set of basis functions including *s*, *p*, and *d* atomic orbitals while incorporating noncollinear and spin-orbit contributions to the Hamiltonian of the system as well as electron correlations at the Hubbard-U approximation as described in our earlier reports.[3,18,19]

Briefly, our numerical procedure is employed as follows:[18] With the chosen classical potential, namely, that of Sutton and Chen,[20] the relaxed geometry of the Ni cluster is obtained at a given temperature using MD. Upon reaching the thermodynamic equilibrium, and, in particular, during the final N_{cl} MD time steps, the TBMDA is employed in order to calculate the MM of the cluster at the geometry provided by the (classical potential) MD at the current time step. That is, at each *i* step of these final N_{cl} steps, the geometry as obtained from the CPOA is used as input to the TBMDA. For this geometrical structure, we run the TBMDA code for a single iteration and calculate the MM of the cluster for a large number N_{ran} of random atomic-spin configurations, from which we obtain the average MM per cluster atom, $\boldsymbol{\mu}_{i,N}(T)$, of an *N*-atom cluster at the given *i*th time step and temperature *T*. In other words, $\boldsymbol{\mu}_{i,N}(T)=(1/N_{ran})\ \Sigma_k^{N_{ran}} p_k(T)\ \boldsymbol{\mu}_{k,i,N}(T)/\Sigma_k^{N_{ran}} p_k(T)$, where $p_k(T)$ is the probability of occurrence of the *k*th spin configuration (of the atomic MMs of the cluster atoms) and $\boldsymbol{\mu}_{k,i,N}(T)$ is the MM per cluster atom during the *i*th time step and at the *k*th random spin configuration. As our final result, $\langle \boldsymbol{\mu}_{i,N}(T) \rangle$, for the $\boldsymbol{\mu}_{i,N}(T)$, we take the absolute value of its thermodynamic average over the final N_{cl} time steps; that is, $\langle \boldsymbol{\mu}_{i,N}(T) \rangle = (1/N_{cl}) |\Sigma_i^{N_{cl}}\ \boldsymbol{\mu}_{i,N}(T)|$. A detailed description of our procedure is reported elsewhere.[18]

Results for $T^{cl}_{C,N}$ and $\langle \mu_{i,N}(T) \rangle$ for Ni_N clusters with $N=43$ (fcc), 80 (fcc), 147 (icosahedral), 177 (fcc), and 201 (fcc) atoms (with ZT structures indicated in parentheses), obtained with the procedure just described, are presented in Figs. 1 and 2, respectively. In these figures, available experimental results are also shown for comparison. In particular, in Fig. 2, the measurements of Gerion *et al.*,[13] for the variation with temperature of the average magnetic moment per

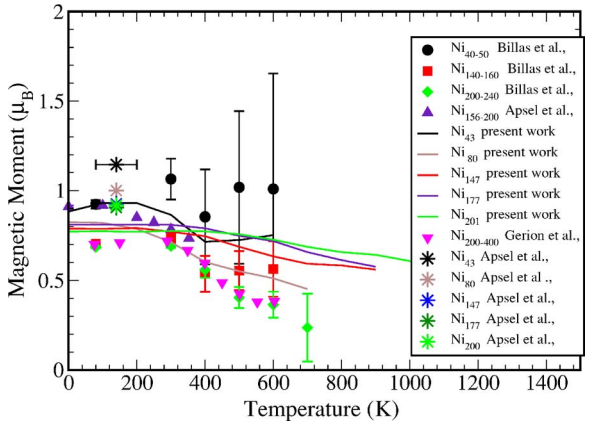

FIG. 2. (Color online) Temperature variation of the average MM per cluster atom for the clusters Ni_N, $N=43$, 80, 147, 177, and 201 as obtained within the present work along with experimental data from Refs. 11–13. The temperature uncertainty in all the results of Apsel *et al.* (Ref. 12) is the same as the one indicated for Ni_{43}.

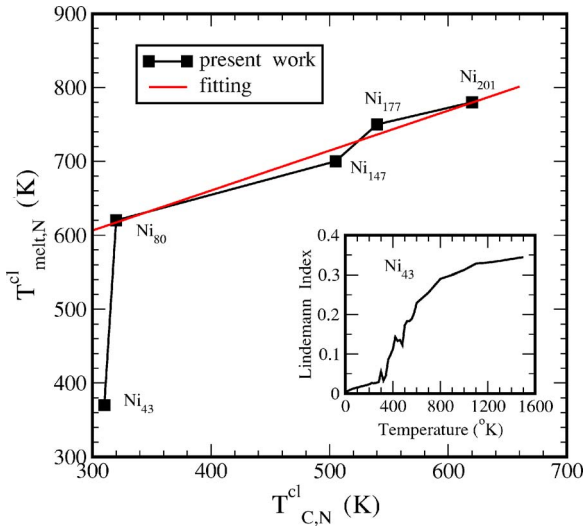

FIG. 3. (Color online) Plot of $T^{cl}_{melt,N}$ as a function of $T^{cl}_{C,N}$ for the Ni_N clusters studied in the present work, N=43, 80, 147, 177, and 201. The Lindemann index for Ni_{43} is shown in the inset (see also Ref. 18).

cluster atom for clusters consisting of 200–240 atoms, are shown along with the experimental results of Billas *et al.*,[11] for Ni clusters of various sizes (having 40–50, 140–160, and 200–240 atoms), and the experimental results of Apsel *et al.*, for Ni_n clusters, n=43,80,147,177, and 200 atoms. Much more limited are the experimental data for $T^{cl}_{C,N}$ and include those of Gerion *et al.*[13] and the estimation of Apsel *et al.*[12] These, as well as the theoretical estimation of $T^{cl}_{C,200-240}$ obtained within the mean-field approximation by Gerion *et al.*, are included in Fig. 1. Worth noting are the large uncertainties in the available experimental $T^{cl}_{C,N}$ data which for Ni_{200}, for example, are within 25% deviation from each other. Within these large experimental error bars (indicated in Figs. 1 and 2), the agreement between the existing experimental data and our predictions is reasonably good. Furthermore, results for the $T^{cl}_{melt,N}$ for these clusters, obtained with the help of the Lindemann index, are also shown in Fig. 1 demonstrating the trend described by Eq. (1).

Fitting the $\langle \mu_{i,N}(T) \rangle$ results to a polynomial, we obtained the magnetic contribution to the specific heat,[13] c_{v,Ni_N}, of the Ni_N clusters by taking the derivative $d\{\langle \mu_{i,N}(T) \rangle\}^2/dT$. The $T^{cl}_{C,N}$ for each one of these clusters is obtained by locating the maximum of $c_{v,Ni_N}(T)$. From these results (see Fig. 1), it is apparent that the Curie temperature of the Ni_N clusters is found to be lower than both T^{bulk}_C and $T^{cl}_{melt,N}$, and increases as the cluster size increases, achieving the bulk T^{bulk}_C value for $N \approx 200$. The similarity in the trends of the variation of both $T^{cl}_{melt,N}$ and $T^{cl}_{C,N}$ as the cluster size increases is very striking. It naturally raises the question of whether a hidden correlation between these two temperatures exists, and if so, whether this could be revealed. This is attempted in the following.

In Fig. 3, $T^{cl}_{melt,N}$ is plotted against $T^{cl}_{C,N}$. From this it is apparent that, with the exception of Ni_{43}, a linear relationship is found to exist between $T^{cl}_{melt,N}$ and $T^{cl}_{C,N}$ for all the clusters studied. A least-square fitting of our results leads to the following quantitative linear relationship:

$$T^{cl}_{melt,N} = \alpha_{fit} T^{cl}_{C,N} + \beta_{fit}, \tag{2}$$

with α_{fit}=0.54 and β_{fit}=443.82. The deviation of Eq. (2) from the results of Ni_{43} can be attributed mainly to the large range of the solid-to-liquid transition temperature found for this cluster as indicated in the inset of Fig. 3. This is reflected in our estimation (370 K) of its melting temperature.[18] (In fact, it can be observed from this inset that if the melting temperature is taken at halfway the rising part of the Lindemann index, then $T^{melt}_{C,N=43}$ is $\approx$600 K and, therefore, lying along the straight line of Fig. 3.) On the other hand, as in the case of $T^{cl}_{melt,N}$, one could have expected the constant α_{fit} to exhibit a weak N dependence.[4,5,7]

Equation (2) leads to the conclusion that $T^{cl}_{C,N}$ exhibits a variation with the number of cluster atoms N similar to that of Eq. (1) for $T^{cl}_{melt,N}$, at least in the major part of the cluster range studied. On the other hand, it should be noted that the mean-field expression

$$T_C = \frac{\gamma n \langle \mu \rangle^2}{3k_B}, \tag{3}$$

where $\langle \mu \rangle$ is the average MM per cluster atom, k_B is the Boltzmann constant, n is the number of atoms (per unit volume), and γ is the Weiss field constant, cannot describe the variation of $T^{cl}_{C,N}$ as a function of N if the parameters n and γ are taken to be N independent. This is because Eq. (3), when applied to the cluster case, leads to the wrong conclusion that the Curie temperature for the cluster, $T^{cl}_{C,N}$, should decrease as the cluster size increases because, as found experimentally, $\langle \mu \rangle$ decreases with the cluster size.

An explanation of the correct variation of $T^{cl}_{C,N}$ with the cluster size can be given if it is assumed that $T^{cl}_{C,N}$ includes different contributions from the surface and the core parts of the cluster due to the variation of the Weiss field and, therefore, of the atomic MM in going from the inner to the outer region of the cluster. Applying the mean-field theory separately to the surface and core regions, and assuming that the surface and core contributions to $T^{cl}_{C,N}$ are proportional to the number of surface and core atoms, respectively, we can easily derive the following expression:

$$\frac{T^{cl}_{C,N}}{T^{bulk}_C} = 1 - \frac{R_{at}}{R^{cl}_N}\left\{1 - \frac{n_{surf}\langle \mu_{surf} \rangle^2 \gamma_{surf}}{n_{core}\langle \mu_{core} \rangle^2 \gamma_{core}}\right\}, \tag{4}$$

where R_{at} and R^{cl}_N are the radii for the Ni-atom and N-atom clusters, respectively, while the indices *surf* and *core* indicate quantities assigned to surface and core parts of the cluster. If it is further assumed that $R^{cl}_N \approx N^{-1/3}$, and taking into account that for small N, $\langle \mu_{core} \rangle \approx \langle \mu_{surf} \rangle$, while for large N, $\langle \mu_{surf} \rangle \approx \langle \mu_{core} \rangle \approx \langle \mu_{bulk} \rangle$, then Eq. (4) can be rewritten as

$$\frac{T^{cl}_{C,N}}{T^{bulk}_C} = 1 - \alpha N^{-1/3}\{1 - \beta e^{-\gamma N} - \delta e^{-\epsilon/N}\}, \tag{5}$$

where α, $\beta\gamma$, δ, and ϵ are fitting constants. Results of Eq. (5) indicate that Eq. (5) can simulate our computational results reasonably well as shown in Figs. 1 and 3.

Our computational results for $T^{cl}_{C,N}$ and $T^{cl}_{melt,N}$, thus, lead to the conjecture that $T^{cl}_{C,N}$ behaves in a way analogous to

$T^{cl}_{melt,N}$. The model description given by Eq. (5) and quantified by Eq. (2) shows that, as in the case of the $T^{cl}_{melt,N}$,[5] the behavior of $T^{cl}_{C,N}$ can be attributed to surface contributions which become quite pronounced as the cluster size decreases. This is reflected in both cases as an $N^{-1/3}$ dependence on the cluster atoms, as dictated by Eqs. (1) and (5).

We have, thus, presented a timely study of temperature-dependent magnetic behavior of Ni clusters and, in particular, the evolution of Curie temperature with the cluster size as it evolves toward the bulk value. The similarity found in the variation of both $T^{cl}_{C,N}$ and $T^{cl}_{melt,N}$ with the cluster size has revealed a linear relationship between the two temperatures, which was justified by model calculations within the mean-field theory applied separately to the surface and core regions of the cluster.

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