RESEARCH ARTICLE

Thermomagnetic Properties of Metal and Metal-oxide Nanoparticles

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Variation of thermomagnetic properties of nanoparticles are the matter of great debate. To develop a suitable model for the study of magnetic properties, the size and shape dependent magnetic properties such as Curie temperature (T_C), Neel temperature (T_N) and magnetization (M_S) of magnetic nanoparticles (Fe, Ni, Co, Fe_3O_4, NiO, CoO, CuO, Ho and $CoFe_2O_4$) have been studied. In the present work, bond energy model has been used with the concept of dangling bond and its effect on the surface of nanoparticles. It is observed that the introduction of packing fraction of materials to this model supports the experimental facts. The obtained results have been explained by considering the concept of dangling bond at the surface of nanoparticle and packing fraction of crystal. It is observed that these magnetic properties decrease with reducing size of nanoparticles and the available experimental data are in good agreement with present theoretical model. The validity of present model encourages us to predict the behaviour of thermomagnetic properties of other nanoparticles.

Introduction

The nanomaterials found the great attention due to their specific and unexpected behavior at their low dimensions. Usually the materials at their nano size shows entirely different behavior from their bulk counterpart [**1-5**]. Nanomaterials have superior optical, electrical, magnetic, mechanical, and thermal properties [**6**], which enable them for a number of applications in various fields. The main parameters affecting these properties, are size and shape [**7,8**]. Nowadays, researchers are working on modifying the properties of nanomaterials so that they can be utilized in various fields of science and technology. Actually nanostructured materials possess excellent properties compared to conventional materials, and this provides them with broad application prospects [**9**]. Thermodynamic properties such as cohesive energy, melting temperature, Debye temperature, melting entropy, melting enthalpy and specific heat of nanomaterials also differ from those of corresponding bulk materials due to the surface effects [**10**]. The elastic properties of nanomaterials like young's modulus, bulk modulus, shear modulus, isothermal compressibility have the completely different behavior at the nano level [**11**]. Also, the optical and electrical properties have different nature at their nano range of size as reported by various researchers [**12**].

In present work, the thermomagnetic properties like Curie temperature, Neel temperature and magnetization of different nanomaterials, has been studied, for which the experimental data are available. The behavior of these properties for some other nanoparticles have also been predicted for which the experimental data are still awaited. Curie temperature (also known as Curie point) is that certain temperature at which certain magnetic materials undergo an abrupt change in their magnetic properties. At Curie temperature, the ferromagnetic material changes into paramagnetic material due to loss of spontaneous magnetization. The Curie temperature of nanoparticles decreases as compared to those of their bulk counterpart. Also the magnetization lowers down on decreasing the size of magnetic materials in the nano range. It is also observed that the Neel temperature of antiferromagnetic material decreases as one move from bulk to nano level of the size. The Neel temperature is that temperature of material at which antiferromagnetic material changes into paramagnetic material. The variation in all these magnetic properties of nanomaterials can be explained on the basis of bond energy model given by Qi with the concepts of dangling bond at surface and packing fraction of materials [**13**].

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Mathematical analysis

Most of the physical properties of solids depend on the bonding between its constituent atoms which are characterized by its cohesive energy. The cohesive energy, defined as the energy required to divide the crystal into individual atoms, of nanoparticle per atom [**14**], is given by

$$E_{nano} = E_{bulk}\left[1-\frac{N}{n}\delta\right] \quad (1)$$

where, N and n are the number of surface atoms and total number of atoms in the nanoparticle, respectively. The term δ denotes the effect of the dangling bonds at the surface and is called relaxation factor. The relaxation factor δ is defined as the ratio of dangling bonds of an atom at the surface to its total bonds. By taking the number of bonds proportional to the surface area of atom, the relaxation factor δ is defined as the ratio of free surface area to the total area of atom at the surface of nanoparticle. In other words 'δ' tells about the nature of surface of nanoparticles.

Using the value of $\frac{N}{n}=\frac{4\alpha d}{D}$ [**14**] in equation (1), and writing the cohesive energy of nanoparticle by Ec(D) and that for corresponding bulk material by Ec (∞), the cohesive energy of a nanoparticle with size 'D' can be written as,

$$E_C(D) = E_C(\infty)\left[1-\frac{4\alpha\delta d}{D}\right] \quad (2)$$

Here, α is shape factor of nanoparticle which is defined as the ratio of surface area of non-spherical particle to the spherical particle of equal volume and is always greater than unity [**15**] and 'd' is atomic diameter.

Again, including the effect of structure of nanoparticle i.e., packing fraction η [**16**], equation (2) becomes

$$E_C(D) = E_C(\infty)\left[1-\frac{4\alpha\delta d}{\eta D}\right] \quad (3)$$

The packing fraction η for a crystal structure is defined as the ratio of volume of total atoms in a unit cell to the volume of unit cell. The value of η [**17,18**] for simple cubic, body centered, face centered, and hexagonal closed packed structure are 0.52, 0.68, 0.74 and 0.74, respectively.

Sun *et.al.*, [**19**] reported that the Curie temperature of magnetic materials is directly proportional to its cohesive energy i.e., $T_C \propto E_C$, using this concept, the expression for the variation of Curie temperature of magnetic nanomaterials with size 'D' can be written as-

$$T_C(D) = T_C(\infty)\left[1-\frac{4\alpha\delta d}{\eta D}\right] \quad (4)$$

Here, $T_C(\infty)$ represents the Curie temperature of corresponding bulk magnetic material. The Neel temperature T_N of antiferromagnetic materials has also the same dependence as the Curie temperature, i.e.

$$T_N(D) = T_N(\infty)\left[1-\frac{4\alpha\delta d}{\eta D}\right] \quad (5)$$

where, $T_N(D)$ and $T_N(\infty)$ are the Neel temperature of the nanoparticle and corresponding bulk material respectively.

Jiang and Lang [**20**] also reported the relation between Curie temperature and magnetization of nanoparticle as

$$\frac{M_S(D)}{M_S(\infty)} = 4\frac{T_C(D)}{T_C(\infty)} - 3 \quad (6)$$

$$\frac{M_S(D)}{M_S(\infty)} = 4\left[1-\frac{4\alpha\delta d}{\eta D}\right] - 3 \quad (7)$$

The proposed model for the prediction of thermomagnetic properties of nanomaterials based on equation (4), (5) and (7) which are obtained by introducing packing fraction η in the model suggested by earlier researchers [**14**].

Results and discussion

In the present work, the variation of cohesive energy E_C(D), Curie temperature T_C(D), Neel temperature T_N(D) and magnetization M_S(D) of different metal and metal oxide nanomaterials such as Fe, Ni, Co, W, Fe_3O_4, NiO, CoO, CuO, Ho, $CoFe_2O_4$ have been studied using the proposed model. The computed results for the prediction of thermomagnetic properties of selected samples are obtained by using equations (3), (4), (5) and (7) described in the section of mathematical analysis. The input data used for the computation of the above-mentioned physical properties are given in **Table 1** and **Table 2**.

The variation of cohesive energy of tungsten nanoparticle with the variation of size and shape, using equation (3), are shown in **Fig. 1**. For tungsten, we have taken the value of relaxation factor δ=1/2. In the case of tungsten nanoparticle, the theoretical curve of cohesive energy for tetrahedral structure is in good agreement with the available experimental data and validates the present model. The results obtained in case of tungsten nanoparticle suggest that it attain tetrahedral structure at its nano level.

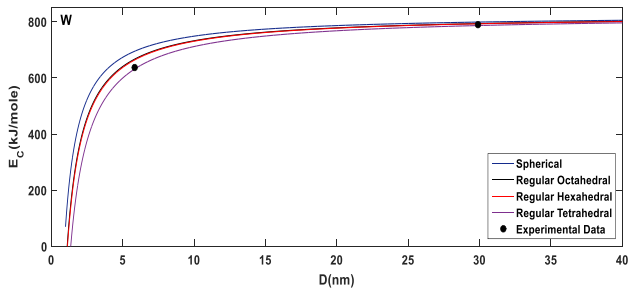

Fig. (1). Variation of cohesive energy E_C of tungsten nanoparticle with size D for different shapes. Solid circles (•) represent the experimental values [**22**].

Table 1. Input parameters for computation [**20,21**].

Material	d (nm)	$T_C(\infty)$ (K)	$T_N(\infty)$ (K)	$M_S(\infty)$ (emu/g)
Ni	0.2492	630	---	48.5
Fe_3O_4	0.2220	860	---	---
NiO	0.8420	---	523	---
CuO	0.6845	---	229	---
Ho	0.7154	---	131.2	---
CoO	0.8520	---	291	---
Co	0.2506	1404	---	143
Fe	0.2482	1043	---	171
$CoFe_2O_4$	0.2264	---	---	75

Table 2. The shape factor for different structure [**15**].

Particle shape	Shape factor (α)
Spherical	1
Regular Octahedral	1.18
Regular Hexahedral	1.24
Regular Tetrahedral	1.49

The variation of Curie temperature of nickel, magnetite, iron and cobalt magnetic nanomaterials with the variation of size and shape along with available experimental values, are shown in **Fig. 2(a) – Fig. 2(d)**. These curves are plotted for the computed results obtained by using equation (4). The experimental values are shown by solid black circles (•).

Fig. 2(a) shows the variation of Curie temperature $T_C(D)$ of *Ni* nanoparticle with the variation of its size at different shapes i.e., spherical (α=1), regular octahedral (α=1.18), regular hexahedral (α=1.24) and regular tetrahedral (α=1.49) shapes. These curves for Curie temperature are plotted using the theoretical model given in equation (4) by considering the value of relaxation factor δ=0.5. In general, it is observed that the Curie temperature $T_C(D)$ of the magnetic nanomaterials decreases with decrease in their size. From the graphs it is obvious that the decrease in the Curie temperature of magnetic nanomaterials is maximum for regular tetrahedral (α=1.49) structure while it is minimum for spherical (α=1) shape. The present theoretical model agrees with the available experimental data [**23**], shown by solid black circles (•). It is observed that the experimental points coincide with the curve for octahedral shape (α=1.18). From this curve, it is also reflected that the Curie temperature $T_C(D)$ becomes almost constant above 80 nm of particle size and becomes equal to that for its bulk material. This variation in Curie temperature of metal and metal oxide nanoparticles can be explained on the basis of molecular field theory proposed by Lang *et.al.*, [**21**].

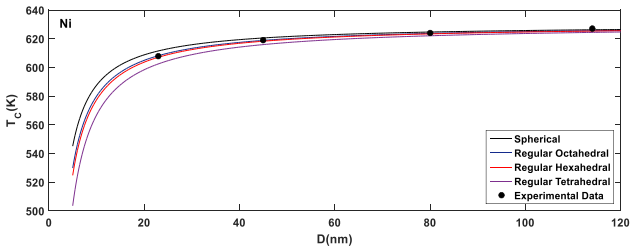

Fig. 2(a). Size dependence of Curie temperature (T_C) of Ni nanoparticle for different shapes. Solid circles (•) represent the experimental values [**23**].

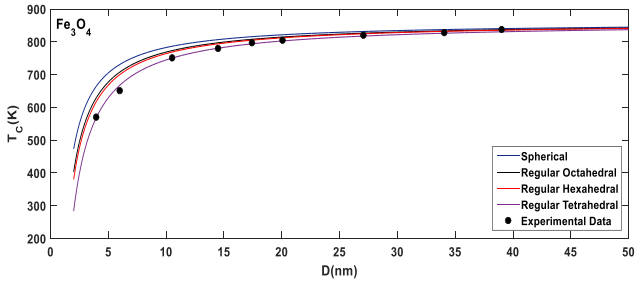

Fig. 2(b). Size dependence of Curie temperature (T_C) of Fe_3O_4 nanoparticle for different shapes. Solid circles (•) represent the experimental values [**20**].

Fig. 2(b) shows the variation of Curie temperature of magnetite (Fe_3O_4) nanoparticle with size at different shapes taking the relaxation factor δ = 3/4. Again it is found the decrease in the Curie temperature with decrease in size of nanoparticle. The agreement of experimental values [**20**] with the theoretical curve predicts that magnetite attains the regular tetrahedral structure (α = 1.49) at its nano level specially below 30 nm. From figure it can also be said that there is a rapid decrease in Curie temperature below 10 nm. Thus, the present model fully explains the variation of size dependent Curie temperature for magnetite nanoparticle.

The agreement of present model with experimental data encourages us to predict the variation of Curie temperature of ferromagnetic nanomaterial iron (Fe) and cobalt (Co). **Fig. 2(c)** and **Fig. 2(d)** represent the variation of Curie temperature of Fe and Co nanoparticle with the size for different shapes. From these figures, one can infer that the Curie temperature decreases rapidly with decreasing size below 40 nm.

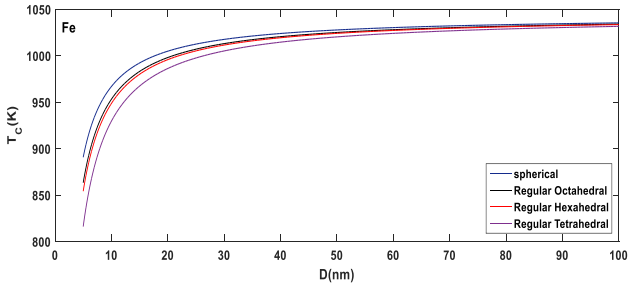

Fig. 2(c). Size dependence of Curie temperature (T_C) of Fe nanoparticle for different shapes.

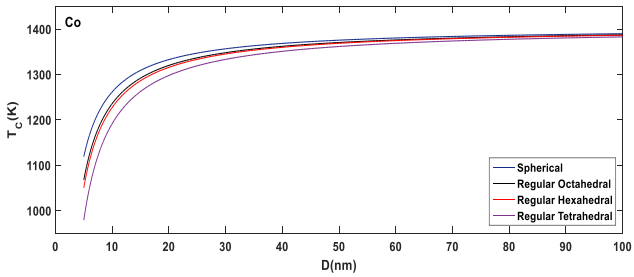

Fig. 2(d). Size dependence of Curie temperature (T_C) of Co nanoparticle for different shapes.

The variation of Neel temperature (T_N) of antiferromagnetic nanomaterials NiO, Ho, CoO and CuO with the size and shape, are shown in **Fig. 3(a)** – **Fig. 3(d)**. The variation of Neel temperature of these antiferromagnetic samples are computed with the help of equation (5) by taking suitable value of parameter δ. The available experimental values are also plotted along with these theoretical curves to validate the present model. The general trend of these curves shows that the Neel temperature decreases with reducing size of nanoparticle as in the case of Curie temperature. This decrease in T_N at nano level is due to high surface to volume ratio and hence more number of dangling bonds at the surface. **Fig. 3(a)** shows the case of nickel oxide (NiO) nanoparticle, in which we have taken δ = 1/2 and size (D) up to 100 nm. From this figure, it is observed that the Neel temperature of NiO nanoparticle decreases rapidly with reducing size below 20 nm. The experimental values [**24**], shown by solid circles (•), are in good agreement with the curve for spherical shape of nanoparticle. The variation of Neel temperature of holmium (Ho) nanoparticle with size at different shapes are shown in **Fig. 3(b)**. In the case of holmium nanoparticle, we have taken again δ = 1/2 and plotted the variation of Neel temperature for the size up to 80 nm. **Fig. 3(b)** confirms that the experimental values [**21**] are in good agreement with the theoretical curve for spherical shape. Thus the present model for Neel temperature, given by equation (5), explains the behavior of holmium nanoparticle at its lower dimension.

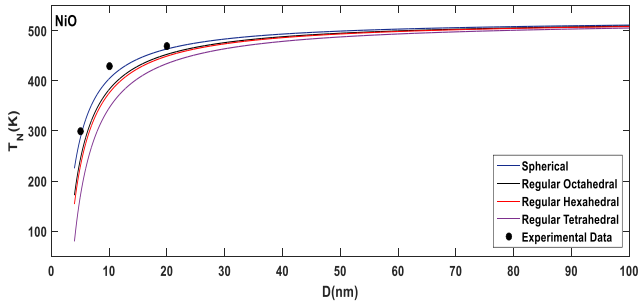

Fig. 3(a). Size dependence of Neel temperature (T_N) of NiO nanoparticle for different shapes. Solid circles (•) represent the experimental values [**24**].

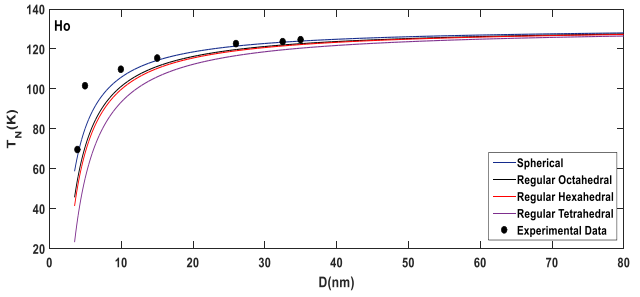

Fig. 3(b). Size dependence of Neel temperature (T_N) of Ho nanoparticle for different shapes. Solid circles (•) represent the experimental values [**21**].

The behavior of Neel temperature for the cobalt oxide (CoO) and cupric oxide (CuO) nanoparticles are explained on the basis of same concept as introduced in the present model and the graphical variation of the Neel temperature with size are shown in **Fig. 3(c)** and **Fig. 3(d)** respectively. In these two cases we have taken the parameter δ=1/4. For the CoO nanoparticle the available experimental data [**21**] coincides with the curve for regular octahedral shape below 6 nm and that of spherical shape above 6 nm. Similarly for CuO nanoparticle, the available experimental data [**25**] coincides with curve for regular octahedral shape. This again validates the present model to explain the specific behavior of nanoparticle at lower dimensions. From all the figures related to Neel temperature, in general, one can conclude that the Neel temperature becomes almost constant above 40 nm which is nearly equal to the Neel temperature of corresponding bulk material.

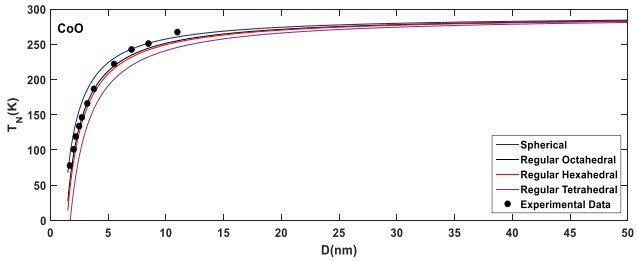

Fig. 3(c). Size dependence of Neel temperature (T_N) of CoO nanoparticle for different shapes. Solid circles (•) represent the experimental values [**21**].

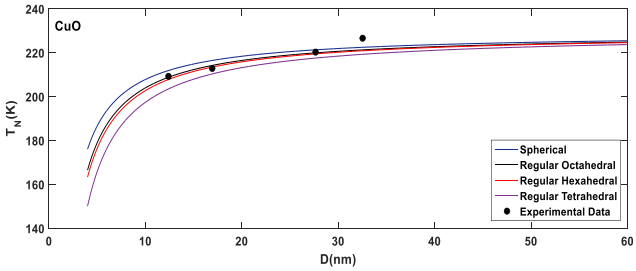

Fig. 3(d). Size dependence of Neel temperature (T_N) of CuO nanoparticle for different shapes. Solid circles (•) represent the experimental values [**25**].

The magnetization of magnetic nanomaterial are found to decrease with decreasing size of nanoparticle. This typical behavior can also be explained on the basis of the concept introduced on present model, formulated as equation (7). As the size reduces to nano level, more atoms reach at its surface and hence they have more numbers of atoms with random orientation of spin. As a result the magnetization decreases at the lower dimension of material. Using this concept of present model, we have computed the magnetization of Fe, Co, Ni and $CoFe_2O_4$ for varying size and shape and plotted in **Fig. 4(a)** – **Fig. 4(d)**.

Fig. 4(a) shows the variation of magnetization (M_S) of Fe nanoparticle with size by considering the value of parameter δ=3/4. It is observed that the experimental values [**20**] has close resemblance with the curve for regular

tetrahedral shape i.e. it should acquire the shape of regular tetrahedral at its nano level. For Co nanoparticle (δ = 0.9), the maximum points of experimental values are in close agreement with the curve for regular tetrahedral shape as shown in **Fig. 4(b)**. This again infers that Co nanoparticle should have the regular tetrahedral shape at its nano level. The same nature of variation in magnetization is found in the case of Ni nanoparticle as shown in **Fig. 4(c)**. For Ni nanoparticle, the magnetization has been computed by taking δ = 3/4. **Fig. 4(c)** suggests that the experimental values of magnetization touch the curves for regular octahedral and regular hexahedral shapes. Thus this present model easily explains the variation of magnetization with size of nanoparticles and gives an idea about the shape of materials at their nano level. Finally, the graphs have also been plotted for the variation of magnetization of $CoFe_2O_4$ with size and shape along with available experimental data [**20**] as shown in **Fig. 4(d)**. This figure shows that the theoretical curve for regular hexahedral shape has close resemblance with available experimental data. This agreement of experimental values with theoretical curve validates the present model. From all the figures related to magnetization, it is observed that there is a remarkable decrement in magnetization of nanoparticle below 50 nm of size, beyond this, the magnetization becomes almost constant equal to the corresponding bulk material.

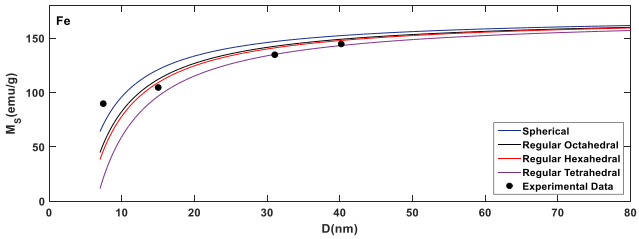

Fig. 4(a). Size dependence of magnetization (M_S) of Fe nanoparticle for different shapes. Solid circles (•) represent the experimental values [**20**].

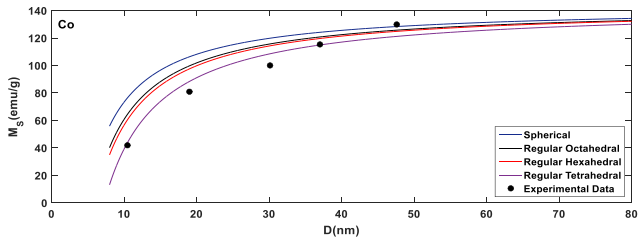

Fig. 4(b). Size dependence of magnetization (M_S) of Co nanoparticle for different shapes. Solid circles (•) represent the experimental values [**20**].

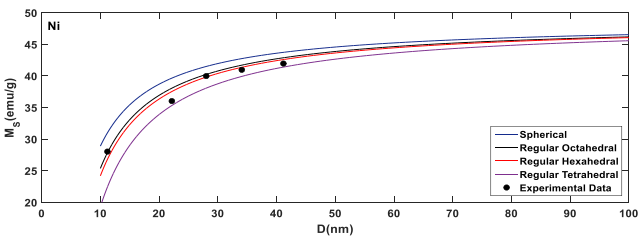

Fig. 4(c). Size dependence of magnetization (M_S) of Ni nanoparticle for different shapes. Solid circles (•) represent the experimental values [**20**].

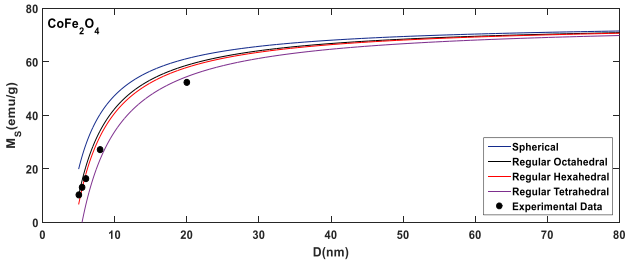

Fig. 4(d). Size dependence of magnetization (M_S) of $CoFe_2O_4$ nanoparticle for different shapes. Solid circles (•) represent the experimental values [**20**].

It is also obvious from the results that the lowering of Curie temperature (T_C), Neel temperature (T_N) and Magnetization (M_S) near room temperature need very low size of transition elements. Although, it is very difficult but in some cases it is possible to achieve. For such materials there will be many possible interesting magnetic applications such as magneto-caloric effect as it is also suggested by Khedr, D. M., *et. al.*, [**26**] and Nagy, Ahmed, *et. al.*, [**27**].

Conclusion

A general model is developed to study the behavior of magnetic nanomaterials at their lower dimensions. This model explains the variation of cohesive energy, Curie temperature, Neel temperature and magnetization with the varying size by considering the concepts of dangling bond at the surface of nanoparticle and packing fraction of crystal. The agreement of present model with the experimental results motivate us to apply this model for the study of the magnetic properties of other nanomaterials for which experimental data need to be developed.

Conflicts of interest

There are no conflicts to declare.

Keywords

Cohesive energy, curie temperature, neel temperature, shape factor, dangling bond.

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