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MAGNETISM OF SMALL TRANSITION-METAL CLUSTERS AND EFFECTS OF ISOMERIZATION

PETER BORRMANN, BERND DIEKMANN, and EBERHARD R. HILF
Department of Physics, Carl v. Ossietzky University Oldenburg, D-26111 Oldenburg, Germany

DAVID TOMÁNEK
Department of Physics and Astronomy, and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI 48824-1116, USA

We investigate the magnetic properties of small transition-metal clusters using a simple statistical model, which requires some input data from *ab-initio* spin-density-functional calculations. In our study, we consider a thermodynamically equilibrated ensemble of clusters with different structures, spin multiplicities, and ground-state energies. We calculate the physical properties of this system by weighting the individual configurations according to the Boltzmann statistics. We find that presence of isomers with very similar ground-state energies, yet very different magnetic properties, gives rise to a rich magnetic behavior of the system which differs significantly from what would be expected for single configurations. We apply the present model to determine the magnetic susceptibility of a cluster ensemble of Langevin paramagnets. Our results show that some of the anomalies in the magnetic behavior of transition-metal clusters might be understood in the framework of our model which is, of course, limited by the extremely high computational effort needed to obtain the input data.

1. Introduction

The magnetic properties of small transition-metal cluster have been of growing interest in the past few years. However, there has not been any study about the dependence on temperature.

As shown in a large variety of papers,[1,2] small clusters exhibit, unlike the bulk, smooth structural transformations, which one might call isomer hopping, and which occur between pure solid and fluid phases over a relatively wide temperature range, in a so-called coexistence phase. In the following we will be concerned with the effect of those properties on the magnetic behavior of clusters. The basic idea is that a cluster of a specific size might have two or more structures with different magnetic moments and that these structures or isomer states occur with their statistical probability.[a] As shown below, this simple assumption causes a strong deviation of the paramagnetic behavior of the magnetic susceptibility from the Curie law. As an interesting feature, a dependence on the strength of an external magnetic field might occur, even at relatively small fields. Transition-metal clusters seem to be natural candidates for the occurrence of such effects because of their different possible electron configurations with very similar energies, which in turn yield quite different average magnetic moments.

2. Theory

We consider n isomers with magnetic moments μ_i and ground-state energies $E_0(i)$, calculated using an appropriate spin-density-functional Hamiltonian. In the presence of an external magnetic field the energy changes. First-order quantum-mechanical perturbation theory yields

$$H_{\rm m} = g\mu_{\rm B} M B_{\rm ext} + \frac{e^2}{8m_{\rm e}} B_{\rm ext}^2 \sum_{\nu} \langle x_\nu^2 + y_\nu^2 \rangle , \quad (1)$$

[a] In the following we will view different configurations, even if they have the same symmetry and only different lattice constants, as different isomers.

where g is the Landé factor and the magnetic field is pointing in the z-direction.[3,4] The first term describes a paramagnet, which will be considered exclusively in the following and can be described with a purely classical description[5] as

$$E_{\mathrm{m}} = -\mu \cdot \mathbf{H}. \tag{2}$$

Now we are able to write down the partition function as

$$Z = \sum_i^n \int_{-1}^{1} d\cos\theta \, \exp[-\beta E_0(i) + \beta\mu_i H \cos(\theta)]$$

$$= \sum_i^n \exp[-\beta E_0(i)] \frac{2}{\beta\mu_i H} \sinh(\beta\mu_i H). \tag{3}$$

Indeed this is an extremely simple partition function, which can be improved to any complexity by adding all degrees of freedom of the clusters, e.g., by substituting the summation over the isomers by integration over the whole configuration space over the atomic positions or by adding a summation over different spin multiplicities of the clusters. From Eq. (3) the average magnetic moment $\langle\mu\rangle$ and the magnetic susceptibility χ can be calculated easily using[5]

$$\langle\mu\rangle = \frac{1}{\beta}\frac{\partial}{\partial H} \ln Z$$

$$= \frac{\sum_i \exp[-\beta E_0(i)] \cosh(\beta\mu_i H)}{\sum_i \mu_i^{-1} \exp[-\beta E_0(i)] \sinh(\beta\mu_i H)} - \frac{1}{\beta H}, \tag{4}$$

$$\chi = \lim_{H\to 0} \frac{\langle\mu\rangle N_{\mathrm{m}}}{VH}, \tag{5}$$

if N_{m}/V is taken as the number of particles per unit volume.[b] In the case of small magnetic fields $\mu H \ll k_{\mathrm{B}}T$ we get

$$\langle\mu\rangle \approx Z_0^{-1}(\beta) \sum_i^n \exp[-\beta E_0(i)] \frac{1}{3}\beta\mu_i^2 H \tag{6}$$

and

$$\chi \approx \frac{N_m}{V} Z_0^{-1}(\beta) \sum_i^n \exp[-\beta E_0(i)] \frac{1}{3}\beta\mu_i^2. \tag{7}$$

[b]The thermal property related to χ by the dissipation-fluctuation theorem is $\gamma = -\frac{1}{\beta^2}\partial_{HH} \ln Z = \partial_H\langle\mu\rangle$.

Here, $Z_0(\beta)$ is the partition function defined in Eq. (3) for zero magnetic field. Equation (7) reveals simply that χ is a linear superposition of the susceptibilities of the individual isomers weighted by their thermal probability.

3. Results and Discussion

The general behavior of the paramagnetic susceptibility according to Eq. (7) is plotted in Fig. 1 for a hypothetical system with only two major isomer states with magnetic moments μ_1 and μ_2 and their energy difference $\Delta E = E_0(2) - E_0(1)$. Unlike a purely paramagnetic behavior according to the Curie law, the plots reveal local minima and maxima. A similar behavior has recently been experimentally found by Cowen *et al.*[6] for Fe_{28} clusters in supercages of NaY Zeolite. The locations of the extrema only depend on the ratio between the magnetic moments μ_1/μ_2 and ΔE. For a given ratio μ_1/μ_2, the position of the minimum depends in an almost linear fashion on ΔE, as can be seen in Fig. 2. The extraordinary sensitivity of these results on ΔE is illustrated by the fact that a change of ΔE by only a few meV moves the minimum by hundreds of degrees Kelvin.

In Fig. 3 the average magnetic moments of the canonical ensemble are plotted for various magnetic fields. These plots reveal the fact that in the presence of a magnetic field the occupation probability of the isomers changes dramatically due to the additional magnetic energy.

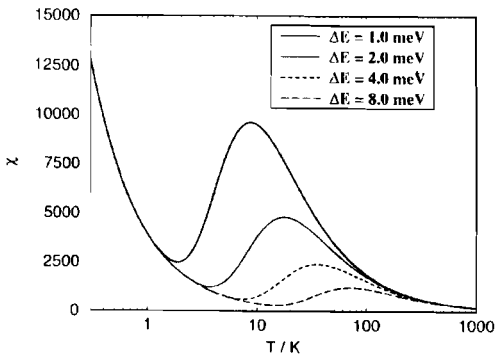

Fig. 1. Magnetic susceptibility $\chi/\mu_{\mathrm{B}}\,\frac{N_{\mathrm{m}}}{V}$ for an ensemble consisting of two magnetic configuration states ($\mu_1 = 1.0\ \mu_{\mathrm{B}}$, $\mu_2 = 10.0\ \mu_{\mathrm{B}}$). ΔE is the energy difference between the two states.

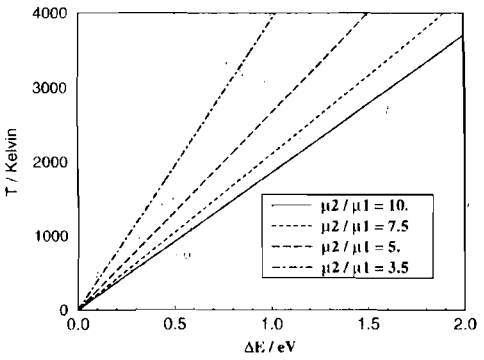

Fig. 2. Location of the local minima of the magnetic susceptibility as a function of ΔE for various ratios μ_1/μ_2 of the magnetic moments.

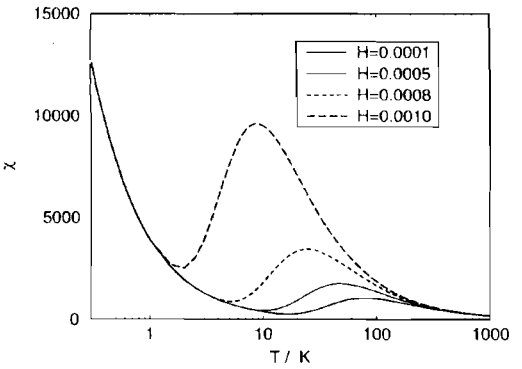

Fig. 4. Magnetic susceptibility $\chi/\mu_B \frac{N_m}{V}$ at nonzero magnetic fields H (eV/μ_B), for ΔE = 0.01 eV, μ_1 = 1.0 μ_B, and μ_2 = 10.0 μ_B.

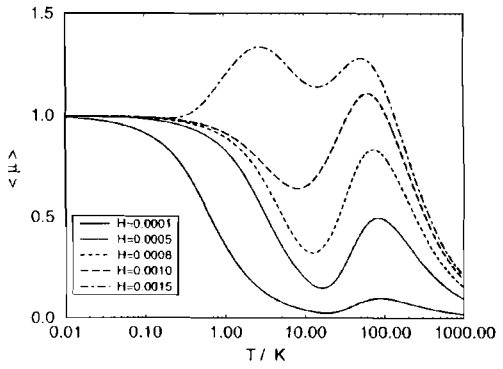

Fig. 3. Average magnetic moments at various magnetic fields H, for ΔE = 0.01 eV, μ_1 = 1.0 μ_B, and μ_2 = 10.0 μ_B.

If one views H to be small in the sense of Eq. (5), the magnetic susceptibility can be easily calculated. For varying magnetic fields this calculation yields a behavior which is very similiar to that of a varying ground-state energy difference (see Fig. 4).

At first sight, configurations of different symmetry — such as bcc versus fcc structures – of Fe clusters seem to be the best candidates to show the effects discussed above. Even if the energy difference between two isomers might be very small, the transition from one isomer to the other may involve a complex concerted motion of atoms and may be associated with a nonzero activation energy. Thus a thermal relaxation might take quite a long time, and a hysteresis might be observable.

Lee and Callaway[7] have found interesting results for Cr_9 and V_9 bcc clusters, which are given in Table I. With varying lattice spacing the average magnetic moment changes by a factor of up to five, whereas the ground-state energy changes are only ≈0.04 Ry/atom. This is especially interesting since even a simple spatial expansion of the transition-metal clusters intuitively is more probable than a structural transformation.

From our results we infer that it is extremely hard to obtain phenomenological results for the magnetic behavior of clusters from spin-density-functional methods, since the results depend very sensitively on ground-state energy differences, which are often very small and comparable in magnitude to the precision of these *ab-initio* methods. In addition, for larger clusters, the number of relevant isomers increases dramatically.

Nevertheless, we have shown that in the model case of two cluster isomers, the rich behavior of the magnetic susceptibility as a function of temperature and the external magnetic field is a sensitive tool to probe structural properties of clusters. On the other hand, once the general magnetic response due to the above discussed effects is understood, one might use the susceptibility of the clusters as a very sensitive thermometer.

Moreover, by applying a sufficiently strong magnetic field, one might be able to suppress one of the

Table I. Average magnetic moments μ (μ_B/atom) and total energy per atom E_{total} (Ry) for Cr_9 and V_9 clusters, as listed in Ref. 7.

Cr_9			V_9		
a/a.u.	μ	E_{total}	a/a.u.	μ	E_{total}
3.82	0.00	−2082.556	4.57	0.33	−1882.202
4.10	0.00	−2082.598	5.14	0.33	−1882.219
4.36	0.67	−2082.779	5.54	0.33	−1882.218
4.63	0.67	−2082.724	5.71	0.33	−1882.213
4.90	0.67	−2082.666	6.28	0.33	−1882.175
5.30	0.67	−2082.651	6.85	2.78	−1882.175
5.45	3.78	−2083.011	—	—	—
6.00	3.78	−2082.934	—	—	—

transition-metal cluster isomers, provided the clusters have ample time for structural rearrangement. An extended study of these effects, including specific examples, will be published elsewhere.

Acknowledgments

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References

1. P. Borrmann, *COMMAT* **2**, 593 (1994).
2. G. Franke, E. R. Hilf, and P. Borrmann, *J. Chem. Phys.* **98**, 3496 (1993).
3. M. Weissbluth, *Atoms and Molecules* (Academic Press, San Diego, 1978).
4. K. Kopitzki, *Einführung in die Festkörperphysik* (Teubner, Stuttgart, 1989).
5. W. Ludwig, *Festkörperphysik* (Akademische Verlagsgesellschaft, Wiesbaden, 1978).
6. J. A. Cowen, K. L. Tsai, and J. L. Dye, *J. Appl. Phys.*, in press.
7. Keeyung Lee and J. Callaway, *Phys. Rev.* **B48**, 15358 (1993).