

Consideration of Schottky Anomaly in the Study of Atom's Orientation in Boltzman Statistics

Morteza Shahbazi Moghaddam

Physics Department of Tehran University and Edinburgh University, UK

Abstract: The target of present undertaken to study the dielectric demagnetization in adiabatic condition, with the consideration of Schottky anomaly, in atom's orientation in Boltzman statistics. We glanced over the generalities on harmonic oscillator and established the statistical sum of classical states, internal energy of oscillating system, and specific heat. In order to study Schottky anomaly in Boltzman statistics, a set of N systems having two degenerated quantified energy levels, at thermal equilibrium, has been considered. The statistical sum of classical states and specific heat have been re-established. In order to study the atom's orientation in Boltzman statistics, a set of N atoms having magnetic moment; μ , at thermal equilibrium and under the influence of a magnetic induction; B_0 , has been considered. The statistical sum of classical states has been established with the consideration of free energy and the entropy of the system. The resultant magnetic moment at high temperatures, showed the Curie law. Having all these data in hand, demagnetization of a dielectric in adiabatic condition has been studied. The network and magnetic entropies were calculated. The study showed that the network entropy could be ignored. It has also been found that the dielectric could be assimilated as a rigid fixed polarized medium, with resultant moment, which was obtained in the study of atom's orientation in Boltzman statistics.

Key words: Schottky anomaly, Boltzman statistics, dielectric, adiabatic demagnetization

INTRODUCTION

The basic magnetic properties of the RE Fe_{12-x} M_x intermetallic compounds (RE=rare earth and M=Mo, Ti, Si, V, W, or Cr) have been studied in depth during the last few years in view of their prospect as basis compounds for permanent magnet materials^[1]. However their performances cannot reach those of other permanent materials such as Nd-Fe-B compounds.

The magnetic structure of these compounds is based on the existence of two magnetic sub-lattices, Fe and rare earth, either ferromagnetically or ferrimagnetically coupled through the 3d-4f exchange interaction. The composition between the magneto crystalline anisotropy of the two sub-lattices can lead to the existence of spin reorientation transition phenomena. The Fe sub-lattice anisotropy is assumed to be of easy-axis type as in YFe₁₁ Ti^[2].

The sign of the second-order crystal-electric-field gradient favors a contribution to the uniaxial anisotropy for RE ions with second order Stevens coefficient $\alpha_2 > 0$ (i.e. RE=Sm, Fr, Tm, Yb). Therefore a spin reorientation transition could be expected for the compounds with $\alpha_2 < 0$ (RE=Nd, Tb, Dy and Ho). However, the observed anisotropic behavior cannot be simply understood

considering only the contribution of the second-ordered terms to describe the RE magnetocrystalline anisotropy. The ErFe₁₁ Ti compound shows a spin reorientation transition at $T_{SR} \approx 60^\circ\text{K}$ from the c axis to a non-collinear magnetic structure at low temperatures, although the Fe and second-order RE contribution favor the c axis as easy magnetization direction in the entire range of temperatures. This fact may be considered as an indication of the relevance of high order crystal electric field terms of drive the spin reorientation transition in these compounds.

In this paper we will focus our study on the demagnetization of intermetallic compounds, which present a complex magnetic behavior with the existence of two spin reorientation transitions in the ferrimagnetically ordered phase. The first spin reorientation transition is of second order and takes place at $T_{SRT} \approx 200-240^\circ\text{K}$ ^[3-5]. Below this temperature the magnetization rotates away from the room temperature easy axis (c axis) to a conical non-collinear magnetic structure in which the easy magnetization direction forms an angle Θ with the c axis.

The second spin reorientation transition occurs at a lower temperature, T_{SR2} , at which the easy magnetization direction reaches the local plane of the tetragonal

structure. A wide range of values for T_{SR2} between 58°K and 120°K has been reported^[3-5]. Ascribed such discrepancies to the different values of the applied magnetic field. Moreover some controversy exists about whether the low-temperature spin reorientation transition is a first- or second-order transition. Hu *et al.*^[4], reported this low-temperature transition as a first order transition. However Andreev *et al.*^[5], interpreted their measurements as a second-order transition at T_{SR2} , in which the magnetization does not reach the basal plane even at 4.2°K.

The main aim of this paper was to review theoretically the demagnetization of intermetallic compounds. In order to accomplish the study, Schottky anomaly in atom's orientation in Boltzman statistics had to be considered. The statistical sum of classical states in different steps has been established. Internal energy and the specific heat were also calculated in different steps. In entropy calculation, it has been verified that the network entropy could be ignored.

MATERIALS AND METHODS

The theoretical calculations have been divided into four steps and each step helps the next to advance and be understood until the main goal is achieved.

Generalities on harmonic oscillator: The Hamiltonian of a linear harmonic oscillator in classical mechanic is^[6]

$$H = P_x^2/2m + CX^2/2 \tag{1}$$

The Hamiltonian equations are;

$$dP/dt = -CX \tag{2}$$

and;

$$dX/dt = P_x/2m \tag{3}$$

(2) and (3) give the movement equation:

$$m d^2X/dt^2 + CX = 0 \tag{4}$$

The solutions are;

$$X = A \cos(\omega_0 t + \Phi) \tag{5}$$

Where;

$$\omega_0 = \sqrt{C/m} = 2\pi\nu_0 \tag{6}$$

This solution is valid for small displacements, in order to calculate the sum of classical states of the oscillator, we know by definition that the statistical sum of classical states is^[7];

$$Z_c = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-H/KT} . dP_x dX \tag{7}$$

$$= \int_{-\infty}^{\infty} e^{-P_x^2/2mKT} dP_x \int_{-\infty}^{\infty} e^{-CX^2/2mKT} dP \tag{9}$$

and;

$$Z_c = 2\pi KT \sqrt{m/C} = KT/\nu_0 \tag{8}$$

At this stage the internal energy U and the specific heat, C, of a group of N identical oscillators at thermal equilibrium and at temperature; T, can be deduced. In fact we can have;

$$\int_0^{\infty} e^{-x^2} dx = \sqrt{\pi}/2 \tag{9}$$

Now, taking Z_c into account, we are able to calculate the internal energy;

$$U = NKT^2 \partial/\partial t. (\text{Log } Z_c) \tag{10}$$

Whereas the specific heat can be deduced as;

$$C_v = NK \tag{11}$$

This is well corresponding to the energy of a system having two degrees of freedom.

From quantum mechanics point of view we can have;

$$E_n = (n+1/2)h\nu_0 \tag{12}$$

Where, ν_0 is the characteristic frequency of oscillator. Taking the sum of classical states, (12), into account, we have;

$$Z = \sum_n e^{-E_n/KT} \tag{13}$$

Therefore;

$$Z = e^{-h\nu_0/2KT} \sum_{n=0}^{\infty} e^{-nh\nu_0/KT} = \frac{e^{-h\nu_0/2KT}}{1 - e^{-h\nu_0/KT}} = \frac{1}{2 \text{Sh}(h\nu_0/2KT)} \tag{14}$$

In case the temperature is quite high, that means;

$$h\nu_0/2KT \ll 1 \tag{15}$$

and finally;

$$Z \approx KT/h\nu_0 \tag{16}$$

Therefore;

$$Z/Z_c=1/h \tag{17}$$

This means that we can, in the space of phase, consider an elementary cell of the length of h , corresponding to Heisenberg uncertainty. Taking Z into account, the internal energy and the specific heat can be calculated;

$$U=(Nh\nu_0/2.)\frac{1+e^{-h\nu_0/KT}}{1-e^{-h\nu_0/KT}} \tag{18}$$

And we can deduce;

$$C_v=NK(h\nu_0/KT)^2\frac{e^{-h\nu_0/KT}}{1-e^{-h\nu_0/KT}} \tag{19}$$

Study of Schottky anomaly in Boltzman statistics: A set of N systems having two non-degenerated quantified energy levels, E_1 and E_2 at temperature T and thermal equilibrium, has been considered. The populations' ratio of these levels is;

$$\frac{N_2}{N_1}=e^{-\delta/KT} \tag{20}$$

Where; $\delta=E_1-E_2$. As, $N=N_1+N_2$, we can deduce that^[8,9];

$$N_1=\frac{N}{1+e^{-\delta/KT}} \tag{21}$$

$$N_2=\frac{Ne^{-\delta/KT}}{1+e^{-\delta/KT}}=\frac{N}{1+e^{\delta/KT}} \tag{22}$$

For the internal energy we have;

$$U=N_1E_1+N_2E_2 \tag{23}$$

If we consider $E_1=0$ and $X=\delta/KT$, then;

$$U=N_2E_2 \tag{24}$$

and;

$$U=\frac{N\delta}{1+e^x} \tag{25}$$

and also;

$$C_v=\frac{X^2e^xNk}{(1+e^x)^2} \tag{26}$$

At high temperatures; $X\ll 1$, therefore;

$$C_v=(NKX^2/4)(1-X^2)=(NKX^2/4)(1-e^2) \tag{27}$$

C_v tends toward zero when X approaches 1. At low temperatures; $X\gg 1$ and;

$$C_v=NKX^2e^{-x} \tag{28}$$

Here also, we can see that C_v tends toward zero when X tends toward infinity.

If we consider N systems with quantified energy levels E_n of degenerescence of g_n , then these levels can be defined as; $E_n=\alpha_n\delta$, in which, α_n is a number between 0 and 1. We considered all the systems at temperature T and at thermal equilibrium and in addition, we considered; $\delta/KT\ll 1$. The sum of classical states of an individual system can be calculated as followings^[10,8];

$$Z=\sum_{n=1}^r g_n e^{-\alpha_n\delta/KT} \tag{29}$$

Regarding the above considerations, then^[6];

$$Z=\sum_n g_n (1-\frac{\alpha_n\delta}{KT}+\frac{1}{2}(\frac{\alpha_n\delta}{KT})^2+\dots) \tag{30}$$

Or again;

$$Z=\sum_n g_n -\sum_n g_n \frac{\alpha_n\delta}{KT} +\frac{1}{2}\sum_n g_n (\frac{\alpha_n\delta}{KT})^2+\dots \tag{31}$$

The internal energy can be calculated from Z ;

$$U=NKT^2\partial/\partial T(\text{Log}Z) \tag{32}$$

Where $\text{Log}Z$, is;

$$\begin{aligned} \text{Log}Z &= \text{Log}((\sum_n g_n) - \frac{\delta}{KT} \cdot \frac{\sum_n (\alpha_n g_n)}{\sum_n g_n} \\ &+ \frac{1}{2}(\frac{\delta}{KT})^2 \cdot (\frac{\sum_n (g_n \alpha_n^2)}{\sum_n g_n} - (\frac{\sum_n (\alpha_n g_n)}{\sum_n g_n})^2)) \end{aligned} \tag{33}$$

The specific heat is then;

$$C_v \approx NK(\frac{\delta}{KT})^2 \frac{1}{(\sum_n g_n)^2} (\sum_n g_n \sum_n (g_n \alpha_n^2) - (\sum_n (\alpha_n g_n))^2) \tag{34}$$

(34) can be used for an individual system with two non-degenerated levels, then it necessitates that;

$$\sum_n g_n = 2, \sum_n (\alpha_n g_n) = 1 \text{ and } \sum_n (g_n \alpha_n^2) = 1 \tag{35}$$

Whereas;

$$C_v = NK \frac{(\frac{\delta}{KT})^2}{4} \tag{36}$$

This shows that we can find the variation of a system with two non-degenerated levels at very high temperature, if we put;

$$\frac{(\sum_n g_n)^2}{\sum_n g_n \sum_n (g_n \alpha_n^2) - (\sum_n (\alpha_n g_n))^2} = 4 \quad (37)$$

Study of atom's orientation in Boltzman statistics: A set of N atoms at thermal equilibrium and at temperature T, has been considered under the influence of a magnetic induction; B₀. It was also considered that each atom possessed a magnetic moment; μ, which could be oriented in parallel or anti-parallel to the direction of B₀. The interaction between the dipoles was supposed to be negligible. Knowing that the magnetic moment energy in a magnetic induction field is; E=±μ.B, therefore the two levels are;

E₁=μB₀ ; with μ anti-parallel to B₀ and E₂=-μB₀ with μ parallel to B₀.

The sum of states is then;

$$Z = e^{-\mu B_0/KT} + e^{\mu B_0/KT} \quad (38)$$

The free energy F_M and the entropy S_M^[6], can be given as;

$$F_M = -NKT \text{Log} Z = N\mu B_0 - NKT \text{Log}(1 + e^{2\mu B_0/KT}) \quad (39)$$

$$S_M = \frac{\partial}{\partial t}(F_M) = NK \text{Log}(1 + e^{2\mu B_0/KT}) - \frac{(2\mu B_0/KT)}{1 + e^{2\mu B_0/KT}} e^{2\mu B_0/KT} \quad (40)$$

The resultant magnetic moment is^[12];

$$M = (N_1 - N_2)\mu = \frac{N}{1 + e^{-2\mu B_0/KT}} (1 - e^{-2\mu B_0/KT})\mu \quad (41)$$

At low temperatures (2μB₀/KT>>1), we have for S_M and M, respectively;

$$S_M \approx NK(1 + 2\mu B_0/KT)e^{-2\mu B_0/KT} \quad (42)$$

$$M = N\mu(1 - e^{-2\mu B_0/KT})/(1 + e^{-2\mu B_0/KT}) \approx N\mu \quad (43)$$

At high temperatures (2μB₀/KT<<1) we will have;

$$S_M = NK(\text{Log}2 - (\mu B_0/KT)^2) \quad (44)$$

$$M = \frac{N\mu^2 B_0}{KT} \quad (45)$$

(45) shows the Curie law^[11].

Application to adiabatic demagnetization of solid dielectrics:

A paramagnetic solid dielectric has been considered for this study. The contributions to entropy are due to; the crystalline network and the magnetism. For crystalline network we were to apply the Einstein approximation model, which assimilates each atom as a harmonic oscillator^[7]. In this case the network entropy of one molecule-gram of the solid is;

$$S_{N_{network}} = -\frac{\partial F_N}{\partial T} = \frac{\partial}{\partial T}(NKT \text{Log} Z_N) = \frac{U}{T} + NK \text{Log} Z_N \quad (46)$$

With;

$$Z_N = e^{-hv_0/2KT} \frac{1}{1 - e^{-hv_0/2KT}} \quad (47)$$

Finally we can get for S_N the following expression;

$$S_N = NK \left(\frac{hv_0}{KT} \frac{e^{-hv_0/KT}}{1 - e^{-hv_0/KT}} - \text{Log}(1 - e^{-hv_0/KT}) \right) \quad (48)$$

Each molecule of solid has a magnetic moment; μ, which can be oriented in parallel or in anti-parallel to the direction of applied magnetic induction B₀. In the absence of external magnetic induction, there exists an internal local magnetic induction; B₁, which reacts on the molecule. B₁ can be ignored when the external magnetic induction is about a Tesla.

At Einstein temperature; θ_E=hv₀/KT=360°K, the internal magnetic induction; B₁, is about 500 gauss and the magnetic moment; μ, is 0.93x10⁻²³ A.m². If we cool the paramagnetic solid down to 1.2°K and adiabatically demagnetize the solid, in the absence of external magnetic induction B, then one can notice that the network entropy of the solid at Einstein temperature is negligible comparing with the entropy due to magnetic induction;

$$S_N \approx NK \frac{hv_0}{KT} e^{-hv_0/KT} = NK(300)e^{-300} \quad (49)$$

The numerical values give for the magnetic entropy;

$$S_M \approx NK \text{Log}2 \quad (50)$$

In which; 2μB₀/KT ≈ 5.62x10⁻² << 1.

The ratio of S_M/S_N is about 3.8x10¹²⁷, which shows that at low temperatures the network entropy can be ignored. From thermodynamic point of view, we can have;

$$dW = dQ - dU = TdS - dU \quad (51)$$

On the other hand we have;

$$S = U/T + NK(\text{Log}Z) \quad (52)$$

and;

$$dS=dU/T-UdT/T^2 \quad (53)$$

Taking (53) into account, (51) will become;

$$dW = -U dT/T + NKT \frac{\partial}{\partial T}(\text{Log}Z)dT + NKT \frac{\partial}{\partial B}(\text{Log}Z)dB \quad (54)$$

In addition we have;

$$U = NKT^2 \frac{\partial}{\partial T}(\text{Log}Z) \quad (55)$$

Inserting (55) into (54), we will get for dW;

$$dW = NKT \frac{\partial}{\partial B}(\text{Log}Z)dB \quad (56)$$

In which Z was;

$$Z = e^{-\mu_B/KT} + e^{\mu_B/KT} = e^{-\mu_B/KT} (1 + e^{2\mu_B/KT}) \quad (57)$$

Inserting (57) into (58), we get finally;

$$dW = N\mu \frac{e^{2\mu_B/KT} - 1}{e^{2\mu_B/KT} + 1} dB \quad (58)$$

If we put;

$$m = N\mu \frac{e^{2\mu_B/KT} - 1}{e^{2\mu_B/KT} + 1} \quad (59)$$

Then;

$$dW=m.dB \quad (60)$$

(60) shows that we can assimilate the solid as a rigid fixed polarization medium with moment of m, which is given by (59).

RESULTS AND DISCUSSION

Demagnetizing a solid dielectric in adiabatic condition necessitated to consider the Schottkey anomaly in atom's orientation in Boltzman statistics. Generalities on harmonic oscillator such as statistical sum of classical states, internal energy and specific heat were reviewed. The statistical sum of classical states was also developed with the consideration of energy from quantum mechanic point of view. It has been verified that at high temperatures the ratio of these two sum of classical states, in the space of phase h. This meant that an elementary cell of the length of h, corresponding to Heisenburgh uncertainty, could be considered. Internal energy and specific heat were re-established, based on this view.

In study of Schottkey anomaly in Boltzman statistics, a set of N systems having two non-degenerated quantified energy levels; E_1 and E_2 , was considered. Taking the populations' ratio of these levels into account, internal energy and specific heat were calculated. The latter was calculated at high and low temperatures and has shown that at high temperatures the specific heat tends toward zero when the difference of energy levels approaches toward infinity.

In order to study the atom's orientation, a set of N atoms at thermal equilibrium and under the influence of a magnetic induction B_0 , was considered. Each atom possessing a magnetic moment μ , could be oriented in parallel or in anti-parallel to the direction of magnetic induction. The magnetic moment energy, in magnetic induction, has been considered. A new definition for statistical sum of classical states was introduced. The magnetic entropy has been calculated, which was based upon the free energy. The final calculation of magnetic entropy resulted in the Curie law.

The above results were applied to the study of demagnetization of solid dielectrics in adiabatic condition. Einstein approximation model, which assimilates each atom as a harmonic oscillator, has been considered. At this stage network entropy had to be calculated, based upon the free energy. With the numerical values, it was verified that the network entropy could be ignored. Finally the necessary work to demagnetize a solid dielectric with respect to resultant moment and magnetic induction has been calculated.

The main aim of this study was to present a step-by-step method of calculation to achieve necessary energy for demagnetizing a solid dielectric.

REFERENCES

1. Buschow, K.H.J., D.B. de Mooij, J.M.D. Mitchell, D. Givord, I.R. Harris and R. Hanitsch, 1989. Concerted European Action on Magnets, Ed. I.V. Mitchell, J.M.D. Coey, D. Givord, I.R. Harris and Hanitsch (London; Elsevier).
2. Hu, B.P., H.S. Li, J.P. Gavignan and J.M.D. Coey, 1989. *J. Phys. C: Solid State Phys.*, 1: 755.
3. Boltich, E.B., B.M. Ma, L.Y. Zhang, F. Pourarian, S.K. Malik, S.G. Sankar and W.E. Wallace, 1989. *J. Magn. Magn. Mater.*, 78: 364.
4. Hu, B.P., H.S. Li, J.M. Coey and J.P. Gavignan, 1990. *Phys. Rev.*, 41: 2221.
5. Andreev, A.V., N.V. Bartashevch, S.M. Razgonyaev, S.S. Sigaev and E.N. Tarasov, 1990. *Physica*, pp: 167, 139.

6. Huang, K., 2001. Statistical Physics. Eds. Taylor and Francis. New York, 40: 144-188.
7. Shahbazi, M.M., 2003a. In Press.
8. Hughes, V.W. and T. Kinoshitie, 1999. Rev. Mod. Phys., 71: 133.
9. Shahbazi, M.M., 2003b. In Press.
10. VanDyke, R.S., P.B. Jr. Schwinberg and H.G. Dehmelt, 1999. Phys. Rev. Lett., 59: 26.
11. Huang, K., 1963. Statistical Mechanics. John Wiley and Sons. New York, 23: 243, 302.
12. Franse, J.M.M. and R. Radvanski, 1992. Handbook of Magnetic Materials Vol. 7, Ed. Bushow (Amsterdam: North-Holland) ch.5.