CHAPTER III

EXPERIMENTAL RESULTS WITH NIOBIUM CLUSTERS

3.1 Deflections at 300 Kelvin. Normal Polarizabilities

Niobium clusters at 300 K behave like normal metal clusters [R. Moro, 2003]. Deflections are proportional to the field intensity squared and the polarizability values are larger than the bulk limit as expected and seen in simple metal clusters [W.D. Knight, 1985]. Figure 18 shows a typical peak deflected by the electric field. Notice that the deflection is only of the order of 40 microns.

Deflections such as the one shown in figure 18 are small, but measurable and the polarizabilities calculated from these results for the range between Nb_3 and Nb_{78} are presented in figure 19. The relatively large uncertainties are primarily caused by the very small deflections due to high speeds at 300 K. This improves as the velocity is reduced.

The fact that these deflections are proportional to the electric field squared is demonstrated in figure 20 where the results of three experiments with Nb_{15} are compared with a quadratic approximation and it fits the data closely.

3.2 Low Temperature Results

The qualitative behavior changes at low temperatures. Figure 21 shows the deflection profiles of some selected clusters at T=300K, 50K and 20 K.

At 50 K, besides the normal deflected component, the clusters also exhibit extended tails. The clusters in these tails are deflected several millimeters as opposed to a few hundred microns for the normal polarizable component of the beam (which correspond to the less deflected peak). Notice that the scale is logarithmic, so the amount of material in the tails is only a small fraction of the total. A significant fraction of the clusters are deflected beyond the detector limits (i.e. more than 4.5 mm).

At 20 K an even larger fraction of the clusters is deflected beyond the spatial range of the detector. We can identify the fraction of the clusters in the normal component of the beam (for example by fitting the peak with a gaussian function) and by subtraction find the fraction that is anomalous. This fraction is shown in figure 21 as parameter "R". The fraction R hence measures the part of the clusters that deflect anomalously (exhibit a permanent dipole).

Another thing that should be noticed is that the tails are single-sided. Although there is some material deflected towards lower fields (for Nb_{11} for example) most of the material in the tails is deflected towards higher fields (which is the right side in these figures).

Experiments at 50 K show that the extension of the tails increases with electric field. An example of this is shown in figure 22 for Nb_{14}. The data has been slightly smoothed for clarity in this figure and it includes four field intensities and also zero field for comparison.

An important feature observed is that the extension of the tails is not proportional to the electric field squared. As shown in figure 23 in the case of Nb_{14}. The linear, rather than quadratic response indicates a permanent dipole moment, so the clusters are ferroelectric.

We calculated the dipole moment associated with the visible extension of the tails. Figure 24 shows these values for clusters in the range Nb_5 to Nb_{32} at T= 50 K.

R measures the fraction of the clusters in the tails (either visible or not), which we call the "ferroelectric fraction". This parameter increases as the temperature is reduced. It also increases when field is increased, but it saturates. When the field is 80 kV/cm most of the losses are saturated (for example when going from 60 kV/cm to 80 kV/cm little material is lost). So at 80 kV/cm the clusters left are basically the ones that behave normally.

We measured deflections of the normally deflected clusters at T=20 K and calculated their polarizabilities. This calculation was done by measuring the average deflection of the clusters that were left and applying equation 16 to get the induced dipole and the definition of polarizability (equation 1). The results are shown in figure 25 where the T= 300 K data is also shown for comparison. A reduction in the polarizability is found, consistent with the prediction for sodium clusters [S.A. Blundell, 2000]. The cases of Nb_9, Nb_{11} and Nb_{14} are special. In those cases there is some material left that is deflected towards lower fields (and which is not swept by the high electric field), so the average deflection is low or negative for those clusters.

The material in the tails (Parameter R) has been measured for several cluster sizes and conditions of electric field and temperature. An example is shown in figure 26 that presents results from two experiments done with niobium at different temperatures but the same electric field.

It can be observed that the ferroelectric fraction is a function of size. There are strong variations for small clusters. For instance Nb_{15} behaves like a normally polarizable cluster even at 20 K, while Nb_{14} has a large ferroelectric fraction. But beyond Nb_{28} all clusters show some ferroelectric fraction. It is also remarkable that beyond Nb_{38} there is a pronounced odd-even alternation, i.e. clusters with even number of electrons have a larger ferroelectric fraction than odd clusters.

To check that the losses where really due to large deflections some control experiments were done. One possibility was ionization of the clusters in the electric field. To rule out this, we used flat deflection plates (which produce a uniform field) that yielded no losses. This experiment also ruled out the possibility of depletion caused by field induced evaporation of helium atoms attached to the clusters.

An experiment covering a larger range of sizes was done and the results are shown in figure 27. The odd even alternations are visible up to 130 atoms. Also it is important to notice that the decay with size is very slow which is an indication that this property is not due to surface effects which would yield a faster decay.

3.3 Simple Model to explain Field and Temperature Dependence

A permanent dipole moment causes deflections according to equation 16, but P_x (the projection of P on the field axis) will depend of how it interacts with the field and the cluster. A model has to be used to calculate the dipole from the deflected peaks. A very successful model developed by Philippe Dugourd and collaborators [P. Dugourd, 2001] applies to a variety of cases. As shown in figure 28 this model correctly describes the response of a molecule with a permanent dipole moment.

However, we cannot use this model to describe our observations. Niobium peaks are deflected asymmetrically and the change in behavior is sudden from deflections of a few hundred microns to several millimeters. Dugourd's model assumes that the dipole is fixed on the cluster axis. Instead, in our model we relax this condition and take into account the tendency of energy levels to avoid crossings.

Our motivation to try this different approach came from [W.A. de Heer, 1991b] where the magnetic deflection of the sodium trimer was explained with the help of a Zeeman diagram. In that case the deflection profile showed two peaks corresponding to the two possible projections of the spin plus an additional peak centered at zero. The reason for that undeflected peak is that the energy levels of different rotational states avoid crossings so they bend and yield a region of very small average slope (the magnetic dipole moment is given by the slope of the energy level).

Similarly in the case of electric dipoles we can construct a Stark diagram [C.W. Townes, 1975] and study the effect of avoided crossings. This is a diagram that presents the energy levels as a function of electric field. Note that the dipole moment is equal to the slope of the energy level (equation 19).

$$P = \frac{\partial W}{\partial E} \tag{19}$$

Notice that the quantum number M_J (projection of J on the electric field axis) is conserved, because the electric field only produces torque perpendicular to itself. Given a certain value of M_J the cluster can be in any state with J more than or equal to M_J and quantum number K (projection of J on the cluster axis). In average these states will be separated by B (the rotational constant). Now, if the dipole moment (P_o) is either aligned or anti-aligned with J the levels will change with electric field according to:

$$W = W_o(J,K) \pm E\frac{P_o M_J}{\sqrt{J(J+1)}} \tag{20}$$

Where the sign will depend on the orientation of the dipole with respect to J. W is the energy and W_o(J,K) is its value at zero field. As the field is increased, these levels will approach and avoid crossing, as shown in figure 29. That will produce two regions. One with very dense anticrossing levels (and zero average slope) and one with downwardly going levels (and large slope). This explains why the change from apparently normal behavior to large dipole moment is so sudden when we increase the electric field. It also explains the single sided deflections observed.

The temperature and field dependence can be calculated by considering the population of rotational energy levels and finding the fraction of the clusters that are beyond the threshold of avoided crossings. Numerically it was found that the fraction could be approximated by the following equation:

$$R = 1 - e^{-\frac{P_o E}{k_B T}} \tag{21}$$

The temperature dependence observed experimentally is stronger however. Besides it was found that R seems to saturate at a given temperature. This indicates that the population that has a dipole moment depends on temperature. The simplest model to fit the observations is to assume that a ground state exists that has a dipole moment and excited states that are normal. If we further assume that the states are equally separated by a constant energy gap the ferroelectric fraction will be given by.

$$R = \left[1 - e^{-\frac{P_o E}{k_B T}}\right]\left[1 - e^{-\frac{T_G}{T}}\right] \qquad (22)$$

Where $k_B T_G$ is the energy gap that separates the states.

This model has only two parameters. An example of fitting to experimental data is shown in figure 30 for Nb_{30} that includes results from 14 experiments.

3.4 Transition Temperatures and Dipole Moments Calculated in the Model

Based on the model proposed we fit the experimental results and get the dipole moment P_o and the transition temperature T_G. Figure 31 shows the dipole moment per atom of niobium clusters. The values are in the order of 1 Debye per atom in the range studied, which are comparable to the best ferroelectrics known [B. Matthias, 1976].

The transition temperatures calculated in the model are presented in figure 32. The maximum is found for Nb_{11} at more than 100 K and it drops and seems to approach a constant value of 10 K for large clusters.

3.5 Stern-Gerlach Experiments with Niobium clusters.

We also did magnetic deflection experiments with niobium clusters [W.A. de Heer, 2003a]. The experimental set-up is similar to the one used in polarizability experiments, only that instead of an inhomogeneous electric field a magnetic field is applied. Deflection profiles in the range Nb_2 to Nb_{13} are shown in figure 33 and figure 34.

Contrary to what has been observed in ferromagnetic clusters [W.A. De Heer, 1990], in this case responses show both, deflections towards high field and towards lower field. Notice that the dimer does respond to the magnetic field, but all other clusters with even number of electrons do not, as predicted from *ab initio* calculations [V. Kumar, 2002]. Clusters with odd number of atoms have one unpaired electron, so they all respond to the magnetic field. Notice that the shapes of the peaks are different from cluster to cluster. In particular, Nb_9 has a stronger response than Nb_7 for example.

As an additional example figure 35 shows the deflection profile for Nb_{22} where the x-axis scale has been converted to magnetic moment. The response of this cluster is almost zero. All even clusters (except for Nb_2) have similar behavior in the range studied (up to about 100 atoms). An example of an odd cluster is shown in figure 36 for Nb_{23}. Many odd clusters show this kind of behavior where a fraction of the clusters seem to be almost no affected by the field while another fraction is strongly deflected.

The shapes of these deflected peaks reflect the fact that we measure the average projection of the magnetic moment on the axis of the field. In the case of the Stern-Gerlach experiment done with atoms we only observe two projections of the spin, but in the case of a cluster the spin is usually coupled to the cluster axis or the rotational angular momentum which give different projections.

Regardless of the kind of coupling the extension of the wings in these peaks is a good measure of the magnitude of the magnetic moment. To measure the extension of the wings we looked for the threshold when the intensity starts to increase. This problem is similar to finding the threshold in the measurement of ionization potential from the ionization efficiency [K.E. Schriver, 1990]. Similarly, we find the intersection between the baseline and the last descent in the signal and compare it to the undeflected peak. The results are shown in figure 37 for clusters in the range Nb_3 to Nb_{52}. The values oscillate about 1 μ_B for odd clusters and zero for even clusters, which means a g-factor of 2 for odd clusters.

The projection of the spin on the field axis depends on the coupling of the spin with the cluster axis and the rotational angular momentum. If the spin is strongly coupled to the rotational angular momentum the spin projection follows equation 23.

$$S_z = \frac{1}{2}\frac{M_J}{\sqrt{J(J+1)}} \qquad (23)$$

Where S_z is the projection of spin on the magnetic field axis, J is the total angular momentum and M_J is the projection of J on the magnetic field axis. This case would yield a deflection profile that would look like a pedestal as shown in figure 38(a). The distribution of magnetic moments would go from minimum to maximum with equal probability. The actual deflection profile would be broader due to the physical width of the undeflected peak.

Another case would be when the spin is coupled to the cluster axis. Then the projection of the magnetic moment would be given by equation 24.

$$S_z = \frac{1}{2}\frac{M_J K}{J(J+1)} \qquad (24)$$

Where S_z is the projection of spin on the field axis, J is the total angular momentum, M_J is the projection of J on the field axis and K is projection of J on the cluster axis. In this case the distribution of angular momentum would be logarithmic (equation 25) and would produce the deflection profile shown in figure 38(b).

$$P(x)\,\alpha\,\log\left(\frac{M_o}{|x|}\right) \qquad (25)$$

Where P(x) is the probability of having the magnetic moment projection x and M_o is the total magnetic moment.

Other possibility is the case where the coupling of the spin is so weak that it can be considered free. This would yield a deflection profile with two narrow projections as shown in figure 38(c). Yet another possibility would be if the spin were in contact with a thermal bath, then the projection would be extremely narrow with only a slight thermal average deflection towards higher field. As shown in figure 38(d).

These four cases could be used to try to fit the observed deflections, but the shapes of the deflected peaks are not clearly one case or another, besides there could be intermediate coupling regimes in which the shapes were different. Instead of using a fitting routine we notice that the second moment of the distribution of magnetic moments is a good indicator of the kind of coupling. The second moment is defined by the following equation:

$$I_2 = \frac{\int_{-M_o}^{M_o} \left(x - \langle x \rangle\right)^2 I(x)dx}{I_o} \qquad (26)$$

Where I(x) is the intensity as a function of magnetic moment and I_o is the total intensity as defined in equation 17. It goes from almost zero for the thermally averaged case to 1 μ_B^2 for the free spin case. Table 1 summarizes this observation.

Table 1: Value of the second moment of the distribution of magnetic moments for several coupling cases.

Coupling case	**Shape of the distribution**	**Second Moment (μ_B^2)**
Coupled to a thermal bath	Narrow	0
Coupled to the cluster axis	Logarithmic	1/ 9
Coupled to the total angular momentum	Pedestal	1/3
Uncoupled	Two projections	1

The effect of avoided crossings has been ignored in these approximations. They would tend to reduce the magnitude of the second moment, but it is not as severe as in the case of electric dipoles. The energy of a magnetic moment of 1 μ_B in a field of 1 T is about 50 times lower than an electric dipole of 20 D in a field of 80 kV/cm, so the density of crossings is less than for the Stark diagram.

As presented in table 1, when the spin is more uncoupled the second moment of the distribution of magnetic moment increases. We can measure this second moment from the experimentally obtained peaks by subtracting the off-peak second moment from on-peak in quadrature. This will give us an indicator of how free the spin is. The results for niobium clusters in the range Nb_3 to Nb_{70} are shown in figure 39. As expected the second moment for the even clusters is zero and the calculated values shown give us an idea of the sensitivity of the measurement. Odd clusters show values as large as 0.24 μ_B^2 and as low as 0.04 μ_B^2 with size dependent variations. These experiments were done at T=20 K for clusters in the range $Nb_{6\text{-}70}$ and at T=33 K for $Nb_{3\text{-}5}$.

3.6 Correlation between Magnetic and Electric Deflection Experiments.

For clusters with odd number of electrons it is possible to compare the second moment of the distribution of magnetic moments with the ferroelectric fraction. The width of the distribution (square root of the second moment) is presented in figure 40 together with the ferroelectric fraction. The correlation coefficient of these two values is 0.41, which is considered moderate. This suggests that the ferroelectric property is related to the uncoupling of the spin.