CHAPTER I
INTRODUCTION

The objects studied in this thesis are very small. A particle of 28 niobium atoms has a diameter of just 1nm, about 20 times smaller than the smallest viruses known. Their study falls in the area of clusters, intermediate between atomic and condensed matter physics. The study of clusters tries to find the evolution of physical properties from the atom to the bulk.

Simple metal clusters have been extensively studied [W.A. de Heer, 1993]. From experiments of mass abundance spectra in sodium [W.D. Knight, 1984] evidence of a shell structure in the electronic levels was found that causes certain sizes to be more stable than others. Closed shells occur at 8, 20, 40 and 58 sodium atoms. Later, evidence of the shell structure was also found in the mass abundance spectra of potassium [W.D. Knight, 1985a], copper, silver and gold [I. Katakuse, 1985]. A property like the ionization potential (IP) shows the transition from atomic to bulk-like behavior. Measurements of IPs in sodium [G. Wrigge, 2002], potassium [W.A. de Heer, 1987] and silver [G. Alameddin, 1992] show high values for small clusters and a downward trend towards the work function (which is the bulk limit) while also showing size dependent variations that can be interpreted by considering the shell structure. The main lesson learned from the study of these simple metal clusters is that they are not exotic and even in the smaller size range they already resemble the bulk and their properties are dominated by the valence electrons.

Ferromagnetic clusters of iron, nickel and cobalt have been studied too [I.M.L. Billas, 1994] [J.P. Bucher, 1991]. It was found that their spin aligns with a magnetic field [W.A. de Heer, 1990], following a thermal averaged behavior as in the case of superparamagnetism [S.N. Khanna, 1991]. The magnetic moments are enhanced with respect to the bulk, possibly due to surface effects. Some rhodium and manganese clusters were found to be ferromagnetic [A.J. Cox, 1993][M.B. Knickelbein, 2001] (Rh is not

magnetic and Mn is antiferromagnetic in the bulk) which shows two cases where properties are unique to small systems, since in both cases the effect disappears with increasing size.

Phase transitions have been observed in clusters. A ferromagnetic to paramagnetic transition has been seen in $Ni_{200-240}$ at T= 340 K [D. Gerion, 2000]. In those experiments the heat capacity was obtained by heating clusters with photons and measuring temperature as a function of energy absorbed. Evidence of a rigid-fluid transition was observed in argon clusters [M.Y. Hahn, 1988]. The melting point and heat capacity of Na_{139} has been determined from the temperature dependence of its photofragmentation mass spectrum [M. Schmidt, 1997]. Also the melting point of tin clusters from measurements of formation energies [T. Bachels, 2000]. A structural phase transition was found in Si_N clusters [M.F. Jarrold, 1991] deduced from drift velocities experiments.
In this thesis we study niobium clusters. Our motivation to choose niobium was that among the pure elements it has the highest critical temperature for superconductivity [C. Kittel, 1996] with the exception of lithium which becomes a superconductor at 20 K, but at high pressures [K. Shimizu 2002].

Superconductivity does not occur in an atom, but it must develop at some point when the particle grows, so we wanted to observe its onset in a cluster. Electron tunneling experiments in aluminum particles [C.T. Black, 1996] as small as 10 nm in diameter still show evidence of the superconducting energy gap (Δ). Nuclear magnetic resonance experiments [K. Nomura, 1980] in aluminum particles showed superconducting features down to 4 nm. Scaling rules tell that the Meissner effect should be suppressed in small clusters [D. Shoenberg, 1962] and indeed our magnetic experiments with niobium did not show evidence of diamagnetism, but only the response of the unpaired electron in clusters with odd number of atoms [W.A. de Heer, 2003a]. Recent experiments of magnetization in small lead particles [S. Reich, 2003] have shown that the transition from diamagnetism to normal behavior happens at the Anderson limit [P.W. Anderson, 1959], that is, when the electronic energy level spacing (δ) is equal to the superconducting energy gap. The

clusters that we study in this thesis are in the ultra-small regime where the energy level spacing is larger than the superconducting energy gap ($\delta > \Delta$).

A straightforward way to investigate the properties of clusters is by measuring their electric polarizability [V.V. Kresin, 1997]. The tool used in this research is a molecular beam machine [G. Scoles, 1988] [W. A. de Heer, 1991a]. The experiment is schematically depicted in figure 1. The principle is simple. Neutral particles pass through a region of inhomogeneous electric field. They become polarized and are deflected towards the stronger field. The goal is to measure this deflection as a function of temperature, size of the cluster and field intensity.

Limited work has been done with metallic cluster beams at low temperature [S. Pokrant, 2000] [D. Gerion, 1999]. Part of this thesis involved the development of a cryogenic source, able to cool the clusters down to T= 9 K.

Our experiments with niobium clusters at low temperatures showed a surprising effect. Many clusters develop a permanent electric dipole moment at low temperatures [R. Moro, 2003]. This thesis presents our results in characterizing this effect. The fraction of clusters that showed large dipole moments was measured at several fields and temperatures. A model is proposed to explain the observations. The study is extended to vanadium and tantalum, that are also superconductors.

Chapter II describes the apparatus, chapter III shows our experimental results with niobium and describes the model proposed. In chapter IV the work is extended to vanadium and tantalum and in chapter V we discuss a possible connection with superconductivity.

1.1 Electric Polarizability of Metal Clusters

A classical perfect conductor in an electric field develops a dipole moment ($\vec{P}$) that cancels the electric field inside the material (see figure 2). This gives rise to a polarizability (α) proportional to the volume of the particle.

$$\vec{P} = \alpha \vec{E} \tag{1}$$

$$\alpha = 4\pi\varepsilon_o R^3 \tag{2}$$

Where R is the classical radius of the particle.

If the particle has N atoms, the polarizability per atom (α_{atom}) will be given by the following equation:

$$\alpha_{atom} = \frac{\alpha}{N} = \frac{1}{N} 4\pi\varepsilon_o R^3 \tag{3}$$

In the bulk limit R^3/N is the Wigner-Seitz radius cubed (R_s^3) so:

$$\alpha_{atom} = 4\pi\varepsilon_o R_s^3 \tag{4}$$

Experiments in sodium clusters show a larger polarizability for the small sizes [W.D. Knight, 1985b] [G. Tikhonov, 2001]. For larger clusters the polarizability approaches the bulk limit given by equation 4. In first order the discrepancy for small clusters can be explained by considering that the electrostatic screening goes beyond the classical boundary of the cluster [N.D. Lang, 1970]. This is due to the spill-out of the electrons which is of the order of 0.13 nm for sodium. Hence the polarizability is modified to give equation 5.

$$\alpha = 4\pi\varepsilon_o (R + \delta)^3 \tag{5}$$

So that the polarizability per atom can be approximated by equation 6.

$$\alpha_{atom} = 4\pi\varepsilon_o \left(R_s + \frac{\delta}{\sqrt[3]{N}} \right)^3 \tag{6}$$

Clearly the correction is more important for small clusters, as seen in experiments [W.A. de Heer, 1993] [V.V. Kresin, 1997]. Figure 3 shows a schematic of this spill out effect, for a cluster of 20 sodium atoms, where the correction to the polarizability is 40%.

A recent polarizability measurement in sodium clusters is presented in figure 4 [G. Tikhonov, 2001]. There are variations in the polarizability superimposed over the spill-out approximation. These variations up to Na_9 have been reproduced almost perfectly by spin-dependent local-density approximation (LSDA) [I. Moullet, 1990]. The spherical jellium model predicts larger polarizabilities of open shell clusters compared to closed shell ones [W. Eckardt, 1984], but underestimates their values by 15%.

A more complicated example of polarizabilities is the case of aluminum clusters, where a deviation from the jellium model was found [W.A. de Heer, 1989]. In particular, the polarizabilities of small clusters are below the jellium value and they recover for clusters greater than Al_{40}.

An experiment with nickel [M.B. Knickelbein, 2001a] showed some clusters whose polarizabilities were significantly larger than the classical ideal value even after considering the spill-out effect (For example Ni_{51} has a polarizability of twice the classical value). These deviations can be explained in part by considering the atomic structures, where closely packed or quasispherical structures show polarizability minima, while structures with "missing" atoms display higher values.

Niobium clusters at room temperature behave like simple metal clusters (as will be seen in chapter III), with larger polarizabilities than the bulk limit that can be approximated in first order by the spill-out effect. That changes at low temperatures.

1.2 Evidence of Permanent Dipole Moments in V, Nb and Ta clusters.

As reported in detail in chapter III, the response of niobium clusters to an electric field at low temperatures is more complex. At T=50K the deflections for some clusters are several orders of magnitude larger than for normal polarizable clusters [R. Moro, 2003].

Moreover, the extensions of these deflections do not follow a quadratic dependence with field, suggesting they are due to permanent dipole moments (a polarizable particle has a quadratic response to the electric field). In contrast, it is predicted [S.A. Blundell, 2000] only a 15% change in the polarizability for sodium clusters between room temperature and T=0 K. A large variation in the polarizability as a function of temperature has been observed in Ge_NTe_M [R. Schäfer, 1996] but never in metallic clusters.

Permanent dipole moments have been seen in clusters and molecules. For example in Ge_2Te and Ge_2Te_2 [R. Schäfer, 1996] and in TiC_{60} [P. Dugourd, 2001], but its observation in niobium clusters contradicts metallic properties. The electrons in a metal would screen any electric field canceling the dipole moment.

Not all niobium clusters have the anomalous property. Some sizes behave normally even at low temperatures, like Nb_{17} for example. For the ones that have the anomalous property there is a fraction that behaves normally at a given temperature. In chapter III we characterize these phenomena.

It is important to notice that these are isolated particles, so even though they come from a source at a very well defined temperature, the distribution of energy states is broad. As an illustrative example, for an ensemble of simple harmonic oscillators the probability of finding one oscillator in state n is given by equation 7, where Δ is the energy gap between levels.

$$P(n) = \frac{e^{-\frac{n\Delta}{K_B T}}}{\sum_{i=0}^{\infty} e^{-\frac{i\Delta}{K_B T}}} = e^{-\frac{n\Delta}{K_B T}}\left(1 - e^{-\frac{\Delta}{K_B T}}\right) \qquad (7)$$

For example if T=20 K and Δ/k_B=10 K, the probability of finding the oscillator in the ground state will be 40%, in the first excited state 24% and so on. Similarly in our experiments the temperature of the clusters ensemble is known, but their states are distributed over a broad range.

As explained in more detail in chapter III, the response of niobium clusters as a function of field is also interesting. The transition from a normal behavior to an anomalous one is sharp. For example, when increasing the field from 20 to 40 kV/cm a fraction as large as 20% of the clusters could go from being deflected a few hundred microns to several millimeters. This is explained in a simple model where energy levels anti-cross in a Stark diagram giving a zero average slope and only when the field is large enough the full slope of the level is realized.

Vanadium and tantalum clusters also show this effect, however it is weaker in both metals. In other words, for them it happens at lower temperatures and higher fields. Other interesting feature of the effect is that it is stronger for clusters with even number of electrons. This has been observed in the three metals studied [W.A. de Heer, 2003b].

Stern-Gerlach magnetic deflection experiments were also done with niobium clusters and we were able to observe the magnetic moment of the last unpaired electron [W.A. de Heer, 2003a]. The g-factors found are all close to 2.0, but the second moment of the distribution of magnetic moments is strongly size dependent. These results are described in chapter III together with a possible correlation with the ferroelectric state.