CHAPTER V

DISCUSSION AND CONCLUSION

Niobium clusters have been studied before, although not at the low temperatures of this work. Mass abundance spectra [V. Kumar, 2001] show magic numbers that are different from the icosahedral growth, suggesting that the electronic structure is the one that determines its growth behavior. Photoionization threshold measurements with $Nb_{4\text{-}29}$ [R.L. Whetten, 1986] show high values for N=8, 10 and 16, that correlates with reactivity toward D_2 [M.E. Geusic, 1985]. In our polarizability experiments at low temperatures, Nb_N clusters that behave normally include N= 8, 10, 15, 16, 17, 19 and 22, so those clusters that have higher ionization potentials are among the ones that behave normally, however there is not a one to one correspondence.

5.1 Possible connection with superconductivity

Experience has shown that properties of the bulk are already visible in clusters, hence we expect to see some signature of superconductivity [M. Tinkham, 1996] in clusters of niobium. Superconductivity has a coherence length associated that for niobium is 38 nm [C. Kittel, 1996]. This is much larger than the typical diameter of the particles studied in this thesis (less than 3 nm). The Anderson limit [P.W. Anderson, 1959], that is when the superconducting gap is equal to the energy level spacing, happens for 7000 atoms in niobium which is also beyond the size range in these experiments. However, the observed ferroelectric behavior could be a precursor to superconductivity and it is supported by the following observations:

- The transition temperatures of ferroelectricity (T_Gs) in niobium clusters tend to 10 K, which is close to the 9.5 K of its superconducting transition. Vanadium and tantalum clusters have lower T_Gs as are their superconducting transition temperatures.

- Our experiments with clusters of manganese, bismuth and cobalt at low temperature show normal metallic polarizabilities and they are not superconductors in the bulk.

- The odd-even effect observed in the three metals favors clusters with even number of electrons. This suggests that pairing is important to the formation of the dipoles. It has been proposed [J. von Delft, 2001], that the presence of an unpaired electron blocks an energy level for pair scattering, reducing the superconducting correlation in small grains.

- Nb_3Al is an alloy that superconducts at 17.5 K and in experiments with binary clusters we found that ferroelectricity in niobium was enhanced with the addition of aluminum atoms.

- The correlation found between the second moment of the distribution of magnetic moments and the ferroelectric fraction suggests that the spin of the last electron uncouple in the ferroelectric state. And conduction electron spin resonance experiments [D.C. Vier, 1983] have shown that the spin relaxation rate is slower in the superconducting state than in the normal state, implying a weaker spin coupling.

Our experiments with lead clusters at low temperatures show that they are normal polarizable particles, so it could be that this property only applies to some superconductors, but the facts just mentioned suggest a connection between these two properties.

This ferroelectric state is a property of the electrons acting collectively because if there were a normal (free) fraction of them they would move to screen any electric field. Based on the theory of hole superconductivity [F. Marsiglio, 1990], it has been proposed [J.E. Hirsch, 2003] that the charge distribution in superconductors is inhomogeneous and it would produce quadrupole moments in clusters with non-spherical shapes. The existence of electric fields inside a superconductor is consistent with this theory as well as the possibility of electric dipole moments, since the ground state wave function would be rigid.

Alternatively, it has been suggested that the anomalous ferroelectricity in niobium could be explained in the electronic ferroelectricity model [C.D. Batista, 2002] [C.D. Batista, 2003] where a system with two dispersive bands with opposite parity plus an inter-band local Coulomb interaction gives rise to an electronic ferroelectric state. Ab initio calculations [G.B. Grad, 2000] show that the valence electron in Nb has the same amount of s and p character, making it a strong candidate for this model. The transition from this state to superconductivity as the particle grows is still an open question.

5.2 Conclusion

A state of the art molecular beam machine was developed that can make cold clusters beams. Temperature can be controlled from 10 K to 300 K. The mass spectrometer in the position-sensitive mode allows the measurement of deflections of the order of 5 microns. This tool allowed us to study electrical polarizability in an uncharted region.

Polarizabilities of small niobium, vanadium and tantalum clusters at room temperature are all higher than the bulk value. They can be approximated by taking into account the spill-out of the electronic cloud. At low temperatures most of these clusters (with some exceptions like Nb_{17}, V_{13} and Ta_{13}) develop dipole moments that are more than an order of magnitude larger than the normal induced ones in fields of the order of 80 kV/cm. These dipoles are comparable to the ones found in the best ferroelectric materials known.

The structure of the cluster is especially important in the small size range were large variations are found, but for larger clusters (beyond Nb_{28} for example) there are less variations and only an odd-even alternation dominates the size dependence. Beyond Nb_{130} this odd-even alternation is not visible in our experiments.

Magnetic deflection measurements show that clusters with even number of electrons have spin zero (except for the dimer) and clusters with odd number of electrons have spin 1/2 with magnetic moments close to 1 μ_B. For niobium clusters with odd number of electrons a positive correlation was found between the ferroelectric fraction and the second moment of their magnetic moment distribution which is a measure of how the spin is coupled to the cluster. This suggests that when a cluster develops an electric dipole moment the spin of the last unpaired electron becomes uncoupled.

The fact that the ferroelectric fraction (and the transition temperature T_G) does not decay for large niobium clusters and the very slow decay in the dipole moment per atom suggest that it is not a surface property. The transition to normal behavior does not happen to at least 300 atoms in niobium. A surface effect that has been predicted for sodium [I.A. Solov'yov, 2002] would yield extremely small dipoles as compared with the ones observed in this work, ruling out that possibility.

The crossover from the ferroelectric to the superconducting state is still to be explored as well as the effect of a magnetic field on the ferroelectric state. Future work in this direction would involve experiments with clusters in the thousand-atom range and simultaneous application of electric and magnetic fields.