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Spin Uncoupling in Free Nb Clusters: Support for Nascent Superconductivity

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Molecular beam Stern-Gerlach deflection measurements on Nb clusters (Nb_N, $N < 100$) show that at very low temperatures the odd-N clusters deflect due to a single unpaired spin that is uncoupled from the cluster. At higher temperatures the spin is coupled and no deflections are observed. Spin uncoupling occurs concurrently with the transition to the recently found ferroelectric state, which has superconductor characteristics [Science **300**, 1265 (2003)]. Spin uncoupling (also seen in V, Ta, and Al clusters) is analogous to the reduction of spin-relaxation rates observed in bulk superconductors below T_c.

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Gas-phase neutral niobium clusters Nb_N ($5 \leq N < 200$) acquire permanent electric dipole moments at low temperatures [1]. This *ferroelectric* state appears to be related to superconductivity [1]. For Nb_N, the observed fraction $R_N(T)$ of those clusters that exhibit ferroelectricity increases with decreasing temperature: $R_N(T) \sim 1 - \exp\{-T_G(N)/T\}$. The ferroelectric transition temperature $T_G(N)$ decreases from $T_G(11) = 110$ K to $T_G(100) \sim 10$ K, while the superconducting transition temperature $T_C(\infty) = 9.5$ K. At low temperatures R_N exhibits a pronounced even-odd alternation, where $T_G(N)$ is *reduced* for an odd-N cluster relative to its even-N neighbors, consistent with observed and expected even-odd alternations in small superconducting particles [2–5]. We have also observed similar effects in Ta, V, and Al clusters [1]. It is unusual for metal particles to exhibit a ferroelectric phase transition. Here we show that the spin coupling properties of these clusters are also anomalous and that the two properties are correlated.

A beam of cryogenically cooled clusters is deflected in a standard Stern-Gerlach magnet [6] to determine their magnetic properties. Recall that the magnetic moment μ of a paramagnetic atom with spin $|S| = 1/2$ aligns or antialigns with the magnetic field of the Stern-Gerlach magnet ($S_z = \pm 1/2$; $\mu_z = \pm 1\mu_B$) and the atom deflects accordingly, as seen in the original Stern-Gerlach experiment on silver atoms [7,8].

Molecular beams of paramagnetic clusters (which include all odd-N clusters of odd-valence metals and clusters of ferromagnetic metals) might be expected to behave similarly. However, it is experimentally found that the spin is coupled to the particle [6,9–12]. This causes the spin to precess about the cluster axes, while the cluster itself rotates [6,9], causing a single essentially undeflected peak ($\mu \sim 0$) rather than two symmetrically deflected $\mu = \pm 1\mu_B$ peaks that result from an uncoupled spin. These averaging mechanisms neutralize the magnetic moments of alkali clusters [6,9] and dominate the magnetic deflections of all ferromagnetic clusters as well [13]. The effect is closely related to spin relaxation in bulk metals [10,11,14].

Consequently, it was expected (and observed) that at room temperature molecular beams of Nb clusters [15] do not measurably respond to the Stern-Gerlach field: the spins are coupled to the cluster framework. At sufficiently low temperatures, however, shoulders appear that symmetrically straddle a central peak of odd-N clusters (Fig. 1). The intensity of the shoulders increases with decreasing temperature. The maximum deflections correspond to $\mu(N) \sim \pm 1\mu_B$ as expected for a free spin as shown in Fig. 2. Hence, these measurements show that the unpaired spin in odd-N Nb clusters is coupled to the cluster framework at higher temperature and that it uncouples from the cluster at low temperatures.

The deflection profiles are analyzed as follows. Let $I_N(B, x)$ represent a profile, where I is the intensity, x is the position, and B is the magnetic field. I is normalized so that $D_0 = \int I(x)dx = 1$. The nth moment of the profile is defined by $D_n = \int x^n I(x)dx$; hence, the first moment represents the average deflection: $D_1 = \int xI(x)dx$ (note that $\int xI_N(B = 0, x)dx = 0$ defines the $x = 0$ position). The second moment of the profile $D_2(B) = \int x^2 I(B, x)dx$ defines the width of the peak. The second moment of the magnetic moment distribution is

$$M_N(T) = [D_2(B) - D_2(B = 0)]/x_1^2,$$

where x_1 is the calculated deflection (in field B) for an N atom cluster with $\mu = 1\mu_B$. $M_N(T)$ is in units of μ_B^2. M_N is found to be independent of B, and M_N directly measures the fraction of the clusters in the beam that are deflected. If the magnetic moment distribution is composed of two components, an uncoupled paramagnetic component with $\mu = \pm 1\mu_B$ and intensity F_N and a coupled component with $\mu = 0\mu_B$ and intensity $(1 - F_N)$, then $F_N = M_N(T)$. If, on the other hand, the magnetic moments are uniformly distributed from $-1\mu_B \leq \mu \leq 1\mu_B$, then $F = 3M_N(T)$ [16]. Simulations of the deflection profiles presented in Fig. 1 show that the latter is the case.

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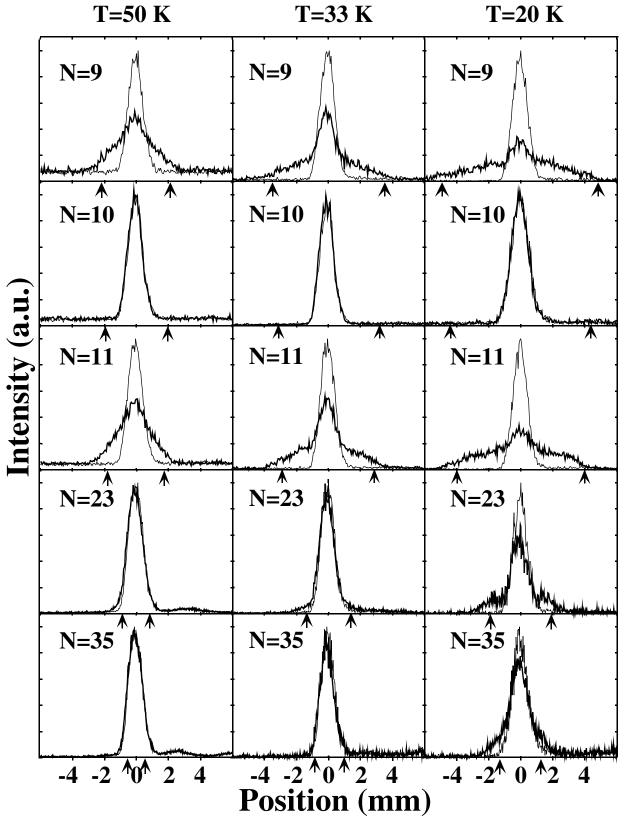

FIG. 1. Representative Stern-Gerlach profiles of Nb clusters at three temperatures. The thin line is without applied magnetic field ($B = 0$) and the bold line is with $B = 0.91$ T and $dB/dz = 3.45$ T/cm. Even-N clusters (besides Nb_2) show no response to the magnetic field; Nb_{10} (second row) is an example. Odd-N clusters do respond, but only at low temperature, where a fraction $F_N(T)$ of the Nb_N clusters deflect symmetrically producing "shoulders" on an undeflected central peak. The arrows indicate the deflections of clusters with magnetic moments of $\pm 1\mu_B$. $F_N(T)$ increases with decreasing temperature: $F_N(T = 300) = 0$ (not shown). Analysis of these deflection profiles reveals that the shoulders are produced by a uniform magnetic moment distribution ranging from $-1\mu_B$ to $+1\mu_B$ (rather than peaks at $\mu = \pm 1\mu_B$). The deflections are inversely proportional to the mass and to the square of the velocity (the velocity of these He carried beams is proportional to $\sqrt{T}$), causing the deflections of a cluster with $\mu = 1\mu_B$ to decrease with increasing cluster size and increasing temperature.

Figure 3 shows the results for Nb clusters at $T = 20$ K. The structure of $M_N(T = 20)$ shows large N-dependent variations. Notably, $N = 9, 11$ are high, while $N = 7, 13–21$ are depressed. M_N rises from $N = 21–29$ followed by a plateau from $N = 29–39$, which is followed by a gradual decrease. These features are reminiscent of those found in the *ferroelectric* fraction at the same temperature determined previously, suggesting that these two properties are correlated. The populations are quantitatively similar if $F = 3M_N(T)$ as shown in Fig. 3. Furthermore, Figs. 3(b)–3(d) show the temperature dependence $M_N(T)$ for three cluster ranges, which also are essentially identical to the ferroelectric fraction for these clusters. [Note that for all clusters $M_N(T)$ vanishes at $T = 300$ K as does the ferroelectric fraction.] These observations suggest that spin uncoupling is associated with the ferroelectric property of the clusters.

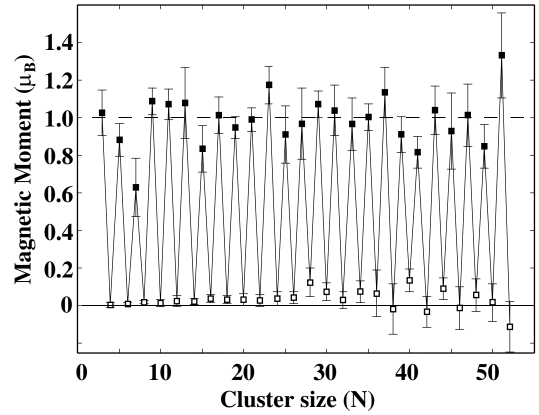

FIG. 2. Magnetic moments of Nb clusters (measured at $T = 20$ K). The magnetic moments are determined from the extent of the shoulders of the deflection profiles (cf. Fig. 1). The odd-N clusters have magnetic moments $\mu_N = 1\mu_B$ (within experimental accuracy) consistent with the magnetic moment of a single unpaired electron. (Only Nb_7 appears to be significantly reduced). Even-N clusters are consistent with $\mu_N = 0$.

The following experiment verifies this hypothesis. We installed the inhomogeneous electric deflection fields used in Ref. [1] upstream from the Stern-Gerlach magnet [Fig. 4(e)]. The collimated cluster beam first passes through the electric field. The ferroelectric clusters are deflected out of the beam when the electric field is activated. The remaining clusters negotiate the magnetic field in the Stern-Gerlach magnet and the emerging beam is detected. Results are shown in Fig. 4 for Nb_{11} and Nb_{13}. When the electric field is off, the deflection profiles show the $\pm 1\mu_B$ shoulders (corresponding reduction of the central peak is clearly observed). When the electric field is activated, the $\pm 1\mu_B$ shoulders diminish. This demonstrates that clusters with an uncoupled spin are ferroelectric as well.

Similar spin uncoupling at low temperatures has also been observed for V, Ta, and Al (which also exhibit low temperature ferroelectricity [1]). Spin uncoupling is not observed in ferromagnetic clusters (i.e., Co) or in Bi clusters which also do not show ferroelectric behavior.

We conclude that only odd-N niobium clusters are paramagnetic due to a single unpaired spin (dimers are exceptions). Whereas the spin is coupled to the cluster at higher temperatures, it uncouples at low temperatures, in which case it behaves approximately as a free spin. Different behaviors of clusters produced in the source at temperature T reflect the differences in internal excitations of the isolated clusters, which are determined by

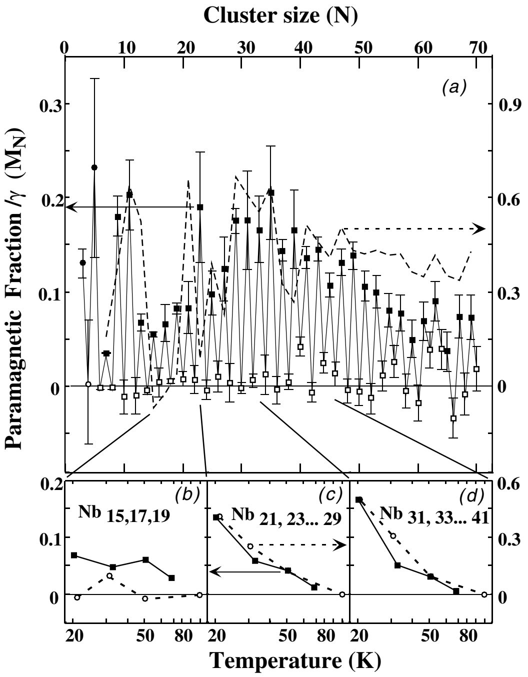

FIG. 3. (a) The paramagnetic fraction $F_N(T) = \gamma M_N(T)$ for Nb_N $(3 \leq N \leq 70)$ at $T = 20$ K, determined from the second moment of the magnetic moment distribution (note that $\gamma \sim 3$; see the text). The odd-N clusters (dark squares, left-hand scale) show significant cluster size dependent variations. Also shown are measurements of the ferroelectric fraction of odd-N clusters from Ref. [1] at $T = 22$ K (dashed line, right-hand scale), which is the fraction of the clusters that have large electric dipole moments at low temperatures. As shown in Ref. [1] the transition temperatures to the ferroelectric state in these clusters is close to the bulk superconducting transition temperature. Here we see that the paramagnetic and ferroelectric fractions are clearly related. (b)–(d) Paramagnetic (dark squares) and ferroelectric (open circles) fractions for several temperatures averaged over three cluster size ranges. Note their similarities. The vanishing of M_N with increasing T indicates that the spin couples to the cluster lattice at those temperatures.

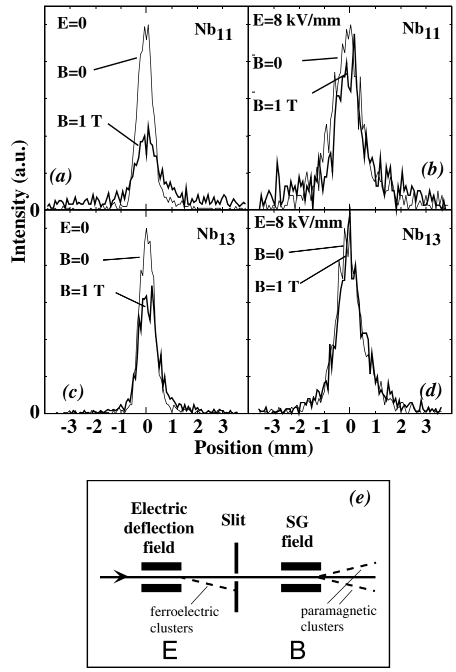

FIG. 4. Two field measurements to investigate the connection between the ferroelectric and the paramagnetic fractions. (e) shows an inhomogeneous electric field (E) followed by the Stern-Gerlach magnet (B). The ferroelectric clusters that are deflected in the electric field are stopped by a collimating slit. The magnet then interacts with the remaining (nonferroelectric) fraction of the beam. Hence, if the paramagnetic clusters vanish when the E field is activated, then this confirms that the ferroelectricity and the spin uncoupling in these clusters are correlated properties. This is found to be the case as demonstrated for Nb_{11} (a),(b) and for Nb_{13} (c),(d). In (a) and (c) the E field is off and the paramagnetic shoulders are observed (note that the peak areas are conserved and the concomitant significant reduction in the central peak is more readily discerned). In (b) and (d) the E field is on and the shoulders are significantly reduced.

Boltzmann statistics of the clusters in the source [17]. Hence, the simultaneous disappearance of the ferroelectric property and the coupling of the spin with increasing temperature indicates that the same excitations are responsible for the disappearance of both.

The coupling of a spin to the cluster is mediated by spin-orbit coupling [6,18,19]. So, apparently, the spin-orbit coupling vanishes at low temperatures.

Conduction electron spin resonance measurements in bulk superconductors [20] show that the spin-relaxation rates reduce below T_C and vanish at $T = 0$. Spin relaxation in pure superconductors is mediated by spin-orbit coupling [21] and its vanishing is due to the depletion of normal electrons below T_C [20,22]. A similar mechanism may be responsible for spin uncoupling in clusters.

Anderson originally argued that when the average level spacing δ, which is inversely proportional to the number of atoms in the particle (roughly E_F/N), becomes of the order of the BCS gap Δ, then superconductivity should disappear [23]. Ralph *et al.* [2] found evidence for a spectroscopic gap that is larger than the average level spacing in small aluminum particles. This gap is driven to zero by applying a suitable magnetic field and the effect was found to depend on whether the particle contains an even or an odd number of electrons. For particles smaller than 5 nm, no trace of the spectroscopic gap was detected.

However, theoretical investigations originally by Matveev and Larkin [3], and others [4,24], revealed that a *parity gap* Δ_P due to superconducting correlations initially decreases with decreasing size, but when $\delta > \Delta$, it again increases. The parity gap [3,4] is defined by $\Delta_P = E_{2l+1} - 1/2(E_{2l} + E_{2l+2})$, where E_N is the total energy of a particle with N electrons, and represents the additional energy of an unpaired electron due to pairing correlations. In a bulk superconductor $\Delta_P = \Delta$, but Δ_P

becomes larger than Δ for very small particles [4], which means that it is an important effect in the energy spectrum of small particles of superconducting materials.

The ferroelectric property points towards a superconducting-like state and electron pairing [1]. The current experiments show a concurrent vanishing of the spin-orbit coupling with the onset of the ferroelectric state. Spin uncoupling is also a property of the superconducting state. Furthermore, recently Hirsch [25] has shown that an electronic charge expulsion effect may accompany superconductivity and suggested a link between the ferroelectric property and superconductivity. Finally, Allen and Abanov [26] have demonstrated the existence of a decoupled electric quantum dipole that results from electronic degeneracy at the Fermi level. It should also be remembered that BCS-like pairing correlations contribute significantly to the binding energies of nuclei [27]. This evidence taken as a whole suggests that the properties we observe result from nascent superconductivity.

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[17] It is important to realize that the source temperature T is reflected in the internal energies of free clusters in the beam. Specifically, the internal energies are fixed in the free clusters, but they are determined by Boltzmann statistics pertaining to the source conditions. For example, a specific harmonic mode of frequency $k_B T_C/h$ will be populated with $n(T) = 1/(\exp T_C/T - 1)$ quanta, i.e., $n(T = T_C) \sim 0.6$. Because of the sparseness of the excitation spectrum, the total energies of clusters produced at a specific temperature and subsequently isolated are broadly dispersed (in contrast to bulk systems). (Note that the Debye temperature of Nb is 275 K and that the average electronic spacing is of the order of the Fermi energy divided by the number of valence electrons, i.e., 50 meV (corresponding to 500 K) for Nb_{20}.) Hence only very few quanta are expected in a cluster at low temperatures. The excitation causing the ferroelectric transition and the vanishing of the spin-orbit coupling must be one of very low frequency and most likely not a rotation (see Ref. [1]).

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