Stern-Gerlach Deflection of Metallic-Cluster Beams

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Supersonic argon beams containing clusters of from 1 to 100 potassium atoms show magnetic deflection patterns with three components: atoms, undeflectable clusters comprising mainly even numbers of atoms, and clusters with odd numbers of atoms. The magnetic moments of the light odd clusters are approximately $1\mu_B$.

The study of small particles requires samples containing reasonable numbers of particles with a narrow size distribution. Since the production of particles involves statistical processes it is difficult to obtain narrow size distributions without some further selection or filtering. This Letter describes a method for producing particles in the intermediate range between well-known molecular species on the one hand, and crystalline solids on the other. The average particle size is controlled by the nucleation conditions. Particles with an odd number of conduction electrons are separated magnetically from the even numbered ones. The smallest odd particles are distinguished from each other according to their magnetic deflections. The particle masses are also estimated by pulse-height analysis of the detected signals.

We report the production and magnetic deflection of beams of metallic clusters of potassium containing from 1 to about 100 atoms. The beam source consists of a conventional oven which discharges into a nucleation chamber containing argon. After nucleation, the clusters are carried out of the chamber in a supersonic jet of argon,[1] passing downstream through a beam skimmer and collimating slits. The beam then passes through inhomogeneous-field deflecting magnets, and the clusters are ionized at the surface of a hot tungsten wire. Individual bursts of ions from the potassium clusters are detected with a multiplier tube. The bursts form pulses of average height proportional to the number of ions in a burst. The average current from the output pulses is recorded as the detector wire is swept across the beam, while a pulse-height analyzer inspects the bursts.

Figure 1 shows two representative curves. The narrower curve is a zero-field beam profile. This profile is identical to the undeflected profile for the atomic beam, save for the fluctuations associated with the large pulses, for which the counting rates are small. The broader curve with magnetic field has three peaks. The outer peaks in the beam profile represent the deflected atoms, which in this run comprise about one-quarter of the intensity of the undeflected beam. These peaks are relatively narrow as a result of the high Mach number and narrow velocity distribution in the supersonic jet. The high central peak has a width at half-maximum which is equal to the undeflected value. However, the width of

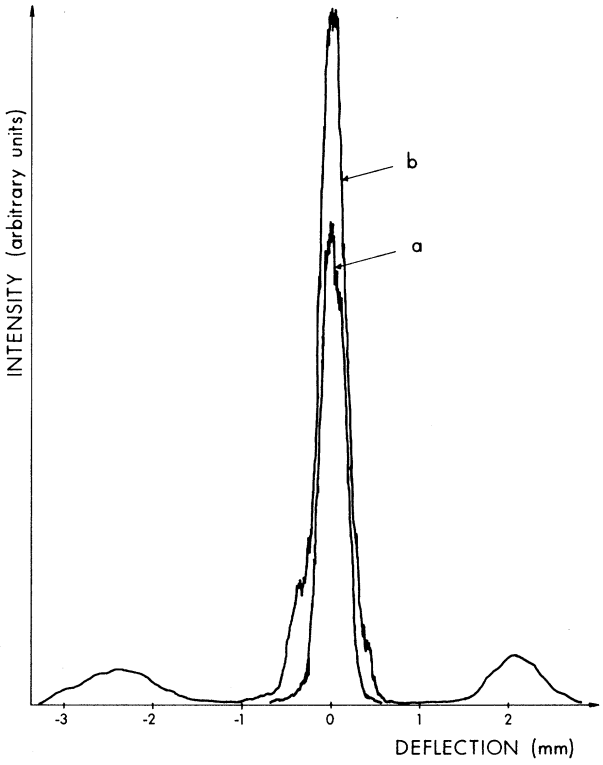

FIG. 1. Experimental cluster-beam intensity vs deflection. Curve a, with field off and curve b, with field on. Nucleation chamber at 600 K, pressure 66 T; nozzle diameter 0.38 mm; undeflected beam half-width at half-maximum 0.17 mm at the detector. Pentamers with magnetic moment of $1\mu_B$ would appear at one-fifth the atomic deflection. This position corresponds to the nearly resolved peaks at the base of the central maximum. The slight asymmetry in the deflection pattern is caused by a variation of magnetic field gradient across the beam, and by the velocity distribution.

the central peak near its base is several times larger. This broadening at the base is symmetrical and proportional to the magnitude of the deflecting field. At high deflecting fields, the height of the central peak is approximately independent of field, indicating the presence of undeflectable particles.[2]

By analogy with the Stern-Gerlach experiment, the deflection of a cluster may be expressed as

$$d_N = K\mu(dB/dz)/Nmv_N^2, \quad (1)$$

where K is a geometrical factor related to magnet length and detector position; dB/dz is the magnetic field gradient transverse to the beam; m is the mass of a potassium atom; N is the number of atoms in the cluster; v_N is the velocity of the cluster; and μ is the total magnetic moment of the cluster, equal to μ_B for $N=1$. We let d_1 be the deflection for atoms in fixed field gradient.

In a first approximation we may treat the metallic clusters as was done[3,4] for larger particles in the ground state at temperatures such that $kT(E_F/N) \ll 1$, where E_F is the Fermi energy of the bulk material, and E_F/N is approximately the energy of the first excitation. In the ground state, the particles with an even number of conduction electrons are in nonmagnetic singlet states; each odd particle contains one unpaired spin and presumably therefore $1\mu_B$.

The calculated [Eq. (1)] and observed values of d_1 agree within 5%, assuming that v_1 equals v_{Ar}, the velocity of the argon. From time-of-flight measurements we find that $v_N \simeq v_{Ar}$ for the lighter clusters, which is consistent with some results in Ref. 1. There is some velocity slip for the heavy particles. Although the trimer is known to possess a magnetic moment from measurements[5] of specimens condensed in a cold rare-gas matrix, the abundance in jet sources is probably small,[6] and we have no definite evidence as yet for their appearance in our experiments. The nearly resolved peaks at $d_1/5$ appear in most of the experimental runs at deflections proportional to the magnetic field. We attribute these peaks to pentamers with magnetic moment of $1\mu_B$. The low intensity in the profile outside of $d_1/4$ is consistent with the very low abundance of trimers and with the absence of velocity slip for $N=5$ (pentamers) and 7 (heptamers).

The mass resolution of the apparatus depends on collimation, deflecting power, and velocity distribution. It is not surprising that the $N=5$ peaks are hardly resolved, since the deflection is of the order of the zero-field linewidth. The apparatus is now undergoing modification which will increase the deflecting power by a factor of 5 and decrease the beam width by a factor of 3. With these improvements, and exploiting the fact that the width of the velocity distribution varies as $N^{-1/2}$, we expect to achieve a mass resolution of around 10% up to $N \sim 20$ by magnetic deflection. Improvements in the detector and in the pulse-height analysis techniques will also permit mass determination to a 10% accuracy up to $N \sim 50$. Available quadrupole mass analyzers could be used[6] in the range $N = 1$–20. The average particle size is controlled by the temperature and pressure of the nucleation chamber.

It is our intention to investigate the electronic spectra of metallic clusters as a function of particle size, using molecular-beam resonance techniques.[7] In addition, a number of microwave resonance experiments are planned to investigate the g values, and hyperfine and spin-orbit interactions,[4,8] for the conduction electrons in small particles, independent of any supporting matrix. The techniques can be applied to a variety of materials, including metals, dielectrics, ferromagnets, superconductors, semiconductors, and alloys. Further experiments are planned involving electric deflections and resonance phenomena.

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Anomalous Spectral and Yield Features of Auger Emission from Symmetric Molecules

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Proton-induced sulfur *LMM* and carbon *KLL* Auger yields from SF_6, CF_4, and CCl_4 gaseous targets are found to be substantially reduced from the corresponding yields observed using H_2S, SO_2, and CH_4. Speculations about the observed dependence on chemical species include inelastic scattering of the Auger electron during its transit out of the molecule and double Auger emission to the continuum.

In this Letter we report the first observation of a significant dependence of the Auger-electron emission cross section on the chemical species of a molecular gas which is ionized by fast protons. We present qualitative arguments for the idea that the Auger electron from a core-location atom undergoes inelastic scattering off neighboring atoms during its path out of the molecule. A discussion of other mechanisms which can lead to our results will also be given. For instance, a high probability of double Auger decay in the symmetric molecules may explain our observations. Previously,[1] small variations ($\lesssim 10\%$) in Auger emission cross section, σ_A, for molecular targets were ascribed to modifications in the Coulomb ionization cross section due to specific molecular environments. We will show that neither ionization-cross-section changes nor variations in fluorescence yields can account for our observations of variations in σ_A for sulfur *LMM* decay from H_2S, SO_2, and SF_6 targets as well as carbon *KLL* emission from CH_4, CCl_4, and CF_4.

These measurements were performed using a Van de Graaff accelerator, a differentially pumped gas cell, a parallel-plate electron analyzer, and an x-ray proportional counter. The accelerator produced proton beams at energies of 0.5, 1.0, and 1.5 MeV that were directed through a 75-mm-diam gas cell and stopped in a Faraday cup. Auger electrons were energy selected by the parallel-plate analyzer and detected by an electron multiplier. Auger yields were measured for all targets at a lab angle of $\theta_L = 160°$. For SF_6 the yield was also measured at $\theta_L = 90°$ where the yield the same as at $\theta_L = 160°$ thus indicating isotropic emission. After correction for the electron-analyzer transmission function,[2] Auger cross sections were determined by comparing sulfur *LMM* and carbon *KLL* yields to a measurement of Ar *LMM* yield, for which the cross section is known.[3] The response of the e^- analyzer from 0 to 500 eV was tested by measuring $p + H_2$ "ejected"-electron energy spectra and comparing to those of Toburen and Wilson.[4] Exact agreement was observed for e^- energies above 10 eV which is adequate for the phenomenon discussed here. Sulfur *L* x-ray measurements were performed by positioning a proportional counter such that it viewed the same interaction region observed by the electron analyzer. All Auger electron experiments were performed with a gas-cell pressure of 1.0 or 2.0×10^{-3} Torr, a pressure region wherein the Auger yields were observed to be *linearly* dependent on pressure. X-ray measurements were performed with a gas-cell pressure of 25×10^{-3} Torr and all yields normalized to that of the Ar *L* x rays, for which the cross section is known.[3]

The principal results of these measurements are shown in Figs. 1(a), 1(b), and Table I. Figure 1(a) illustrates sulfur *LMM* Auger spectra for SF_6 and SO_2, which have not been corrected for the E^{-1} (E is analyzed electron energy) analyz-

