

Electron Localization in a Disordered Insulating Host

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Transport of excess electrons has been studied in solid N_2 -Ar mixtures between 5 and 60 K using muon spin rotation in magnetic and electric fields. At low temperatures, orientational frustration of N_2 molecular quadrupoles by a sufficiently high concentration of Ar atoms leads to formation of a quadrupolar glass phase in which electrons are found to be strongly localized. This feature is in marked contrast to the electron delocalization observed in the low-temperature α phase of pure solid nitrogen, which shows long-range orientational order.

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Most of our understanding of electron transport in solids is modelled on nearly perfect crystalline materials, but even in this limit disorder plays a crucial role [1]. The most familiar phenomenon governing electron transport in disordered *metals* is "Anderson localization" [2,3]: introduction of sufficiently strong disorder into a metallic system causes spatial localization of electron states near the Fermi level and thus drives a transition to an insulating state (the Anderson transition). In metals, however, electron-electron interactions dramatically modify the density of states at the Fermi level, leading to formation of the Coulomb pseudogap [4]. To observe the effects of disorder on electron transport without the complications of electron-electron interactions, one must therefore study electron dynamics in a disordered *insulating* host.

A special class of solids formed by random mixtures of molecular and atomic species [5] offers a unique opportunity for such studies. *Pure* molecular crystals such as solid N_2 or CH_4 undergo an order-disorder phase transition from the "plastic crystal" high-temperature phase (where the multipole moments associated with the molecules can rotate more or less freely) to a low-temperature phase with long-range orientational order. This order is severely frustrated by the random substitution of spherical atoms or molecules (e.g., Ar in N_2 , Kr in CH_4 , or para- H_2 in ortho- H_2 etc.); strong enough dilution generally leads to a new type of phase called an *orientational glass* in which the multipole moments are "frozen" in random directions [5].

One of the best studied orientational glass systems is the N_2 -Ar mixture [6]. Pure N_2 has two low-pressure

crystalline forms, the hexagonal close-packed (hcp) high-temperature phase and the cubic $Pa3$ (fcc) low-temperature phase. Despite intrinsic geometrical frustration, pure N_2 undergoes a first-order phase transition to a long-range periodic orientationally ordered α phase below $T_{\alpha\beta} = 35.6$ K [7]; the high-temperature β phase is orientationally disordered. Solid $(N_2)_{1-x}Ar_x$ is obtained by simply cooling liquid mixtures, as nitrogen and argon are completely miscible. The hcp sites are randomly occupied by N_2 and Ar. As the Ar concentration x is increased, the hcp-to-fcc transition temperature decreases. Above the critical Ar concentration $x_c \approx 0.23$, the hcp lattice appears to be stable down to $T = 0$. The dynamical orientational disorder of the high- T phase eventually freezes into a static pattern of randomly oriented N_2 molecules, the *orientational glass* [6]. Heat-capacity [8], neutron scattering [9], and x-ray diffraction [10] measurements support the model of a gradual freezing of the orientational degrees of freedom. One can gradually change the local order parameter and even switch the disorder on and off by changing the temperature and/or Ar concentration. These features make N_2 -Ar mixtures very convenient systems for studying the effect of disorder on electron transport.

The low-temperature heat capacity in the glass phase of N_2 -Ar shows a term linear in T and an enhanced T^3 term [8], akin to the "two-level system" behavior observed in amorphous solids. Unlike the situation in spin glasses, where spin-lattice coupling may be negligible, in orientational glasses the orientational degrees of freedom are strongly coupled to lattice displacements: reorientation

of a multipole moment involves changes of atomic coordinates. Because of this coupling, orientational glasses exhibit transport properties analogous to those of translational glasses similar to amorphous SiO₂.

Being a mixture of insulators, the N₂-Ar system has a very large energy gap (~ 10 eV), so that even at high temperature the ambient density of free electronic states is exponentially low. Experimental study of electron transport in this system therefore requires that the empty conduction band be “injected” with free carriers, ideally in low enough concentrations that electron-electron interactions can be safely ignored. The ionization of molecules and/or atoms by high energy charged particles (e.g., positive muons) offers just such a source of free carriers.

In a typical muon spin rotation/relaxation (μ^+ SR) experiment [11], one accumulates a time spectrum by detecting the arrival and subsequent decay of spin polarized 4 MeV positive muons (μ^+) stopped in the sample one at a time. Each incoming muon leaves behind an ionization track of excess electrons and ions. Recent μ^+ SR experiments in liquid helium [12], liquid and solid nitrogen [13–15], liquid [16] and solid neon, and argon [17] have shown that the spatial distribution of these ionization-track products is highly anisotropic with respect to the final position of the muon: the μ^+ generally thermalizes well “downstream” from its last ionization event. Some of the excess electrons generated in the end of the μ^+ track turn out to be mobile enough to reach the thermalized muon and form the hydrogenlike muonium ($\text{Mu} \equiv \mu^+e^-$) atom.

This phenomenon of *delayed muonium formation* (DMF) is very sensitive to the *electron mobility*—a free electron in the conduction band will quickly reach the μ^+ , whereas an electron that undergoes *localization* to become a *polaron* will arrive much later, if at all. (Typical mobilities in insulators range from about 10^{-3} – 10^{-2} cm² V⁻¹ s⁻¹ for localized electrons to about 10^2 – 10^3 cm² V⁻¹ s⁻¹ for delocalized electrons.) Thus DMF forms the basis of a new technique for measurements of the electron mobility b_e in insulators [14–16] and semiconductors [18,19] on a *microscopic scale*: b_e can be estimated whenever one can measure both the characteristic time for Mu atom formation τ and the characteristic distance between the stopped muon and its last radiolysis electron R . The former is determined from the magnetic field dependence of the muonium signal amplitude and phase, using the coherence criterion for Mu formation [14]. The latter is extracted from the dependence of the muonium formation probability on applied electric field—basically, a sufficiently high applied electric field will overcome the Coulomb attraction between the muon and electron. The characteristic distances involved are typically on the order of 10–100 nm; the characteristic time for the electron to reach the muon ranges from $\tau < 10^{-10}$ s

for delocalized electrons to $\tau > 10^{-6}$ s for localized electrons [17]. In the simplest case of viscous motion, the parameters involved are connected by the following expression [14]:

$$\tau = \frac{R^3 \epsilon}{3eb_e}, \quad (1)$$

where $-e$ is the electron charge and ϵ is the dielectric constant of the medium.

The potential of the μ^+ SR-DMF technique for electron mobility measurements in solids was first demonstrated for pure solid nitrogen [14]. Excess electrons were found to be *delocalized* in α -N₂, which shows a long-range orientational order. In this Letter, we present evidence for strong *electron localization* due to *orientational disorder* induced by Ar impurities in the low-temperature orientational glass phase of solid nitrogen-argon mixtures.

The experiments were performed on the M20 beamline at TRIUMF and on the EMU beam line of the ISIS Pulsed Muon Facility at the Rutherford Appleton Laboratory. In each experiment, mixtures of ultrahigh purity N₂ and Ar (less than 10^{-5} impurity content) were condensed from the gas phase into a liquid. At ISIS, the sample cells were 25 mm in diameter and 5 mm thick; at TRIUMF, they were 18 mm in diameter and 4 mm thick. Solid samples were carefully grown from the liquid phase at a typical speed of about 5 mm/h under a vertical temperature gradient of about 2 K across the cell. At both laboratories, positive muons of 28 MeV/c momentum and 100% spin polarization were stopped in the samples and μ^+ SR time spectra were recorded at various different temperatures and applied magnetic and electric fields. (The time differential μ^+ SR technique relies on positrons from the muon decay being emitted preferentially along the direction of the muon polarization and is described in detail elsewhere [11].) The resultant muon decay asymmetry $A(t)$ directly reveals the time-dependent amplitudes of the characteristic precession signals of paramagnetic (Mu) and diamagnetic (μ_D) species, both of which are present in all (N₂)_{1-x}Ar_x mixtures studied.

In a strong transverse magnetic field, the muonium precession frequency splits into two triplet Mu signals [11]; but in weak (< 10 G) field these two triplet Mu signals are nearly degenerate, giving a single muonium precession frequency $\omega_{\text{Mu}} \approx -103\omega_\mu$, where $\omega_\mu/2\pi \approx 0.01355$ MHz/G. Thus, Mu and μ_D signals are easily distinguished.

The μ_D signal sometimes exhibits two components: one which is slowly damped due to random local fields from ¹⁴N nuclear moments and one which disappears much faster due to *very* delayed Mu formation. The latter is observed only in cases where the electrons form polarons which are still mobile enough to reach the μ^+ on a μ s time scale. The general form of the μ^+ SR asymmetry spectrum is therefore

$$A(t) = A_{\text{Mu}} e^{-\lambda_{\text{Mu}} t} \cos(\omega_{\text{Mu}} t + \phi_{\text{Mu}}) + A_S e^{-\lambda_S t} \cos(\omega_{\mu} t + \phi_D) + A_F e^{-\lambda_F t} \cos(\omega_{\mu} t + \phi_D), \quad (2)$$

where A_{Mu} , ϕ_{Mu} , and λ_{Mu} are the amplitude, initial phase, and relaxation rate for the muonium signal, and the corresponding quantities with S and F subscripts parametrize the “slow” and “fast” decaying μ_D signals, which have a common initial phase ϕ_D . The sum $A_D = A_S + A_F$ defines the net diamagnetic asymmetry. Muonium relaxation is caused by its nuclear hyperfine interactions [20].

Figure 1 depicts the temperature dependences of the asymmetries (amplitudes) of the various signals in solid $(\text{N}_2)_{1-x}\text{Ar}_x$ for $x = 0, 0.09, 0.16$, and 0.25 . At high temperature (above about 40 K), all the mixtures have roughly the same Mu and μ_D asymmetries as pure N_2 . At low temperatures, however, adding argon causes dramatic changes. In pure N_2 below about 30 K, there is a large Mu signal and a small μ_D signal, indicating efficient DMF; as Ar is added there is a progressively larger μ_D signal, indicating reduced DMF, until at $x = 0.25$ there is only a small Mu signal. The increase in Mu amplitude is only half the corresponding decrease in μ_D amplitude because half the Mu polarization oscillates at the muonium hyperfine fre-

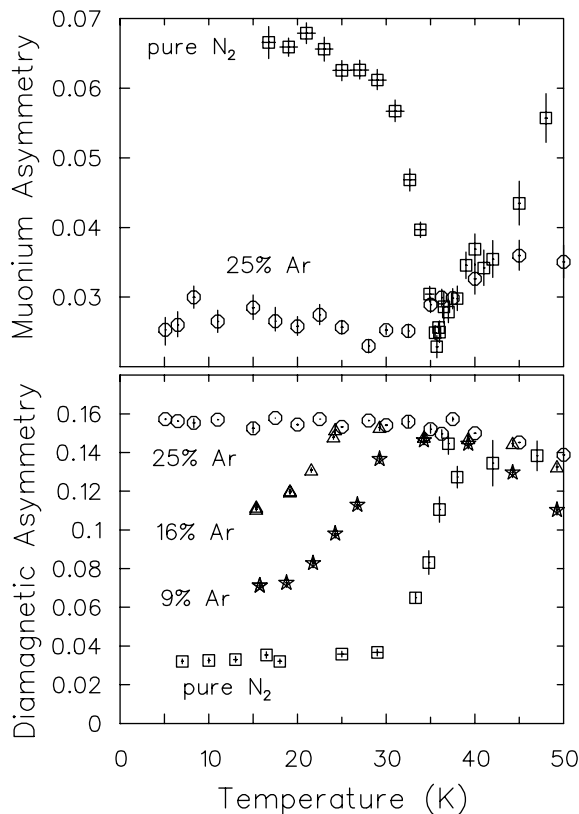


FIG. 1. Temperature dependences of muonium (top, $H \approx 5$ G) and net diamagnetic (bottom, $H \approx 100$ G) signal amplitudes in pure solid nitrogen (squares) and solid $(\text{N}_2)_{1-x}\text{Ar}_x$ (circles: $x = 0.25$; triangles: $x = 0.16$; stars: $x = 0.09$).

quency and appears depolarized [11]. Full asymmetry is about 0.19 in these experiments.

In solid N_2 , muonium formation has been shown [14,15] to proceed via two channels: the thermal DMF process outlined above and the epithermal *prompt* process which takes place prior to the μ^+ thermalization and is therefore independent of temperature, electron mobility etc. The small, temperature independent Mu amplitude in the $x = 0.25$ sample (see Fig. 1) is the same as the *prompt* Mu amplitude in pure solid nitrogen [15], suggesting a complete absence of DMF in the orientational glass.

The hypothesis that Mu formation in the $x = 0.25$ mixture is essentially all via the *prompt* (epithermal) channel at 20 K is further supported by the observation that A_{Mu} and A_D do *not* depend on an externally applied electric field for that sample, as shown in Fig. 2. Both amplitudes show significant electric field dependence in pure N_2 at 20 K, from which the characteristic muon-electron distance R is estimated to be about 50 nm [14,15]; about the same value of R is found in solid Ar, which exhibits almost 100% DMF [17]. The fact that solid N_2 and solid Ar have similar values of R is not at all surprising, since N_2 molecules and Ar atoms have about the same size and about the same ionization potential [21] and therefore about the same cross section for muon (or Mu atom) scattering. It is therefore natural to expect that R is about the same in mixtures as in the pure substances. The absence of DMF at this length scale at low temperature in the $x = 0.25$ mixture suggests that electrons are *localized* in this orientational glass.

One might suspect that it is the difference between lattice sites randomly occupied by N_2 molecules and Ar atoms which acts as a localizing influence, for example, by simple scattering (or even trapping) of initially delocalized electrons by Ar impurities. However, Fig. 1 shows

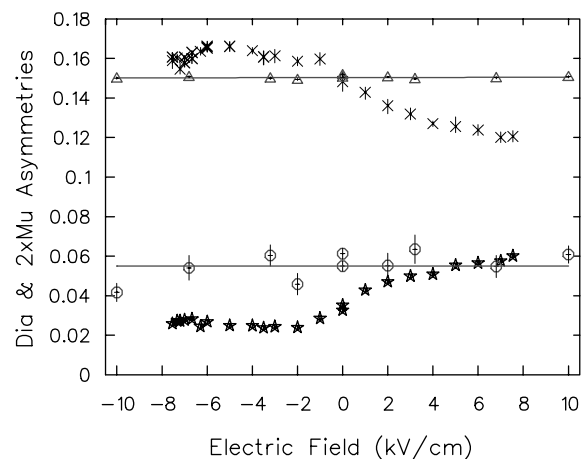


FIG. 2. Electric field dependences of $2 \times A_{\text{Mu}}$ and A_D in pure solid nitrogen (crosses and stars, respectively) and in solid 75% $\text{N}_2 + 25\%$ Ar (circles and triangles, respectively) in a transverse magnetic field $H = 36$ G at $T = 20$ K. The muonium amplitudes are doubled to compensate for the 50% depolarization of Mu by hyperfine oscillations [11].

that mixtures without sufficient Ar concentrations to destroy orientational order at low temperature still exhibit efficient DMF; this process requires *delocalized* electrons. Scattering of these electrons by Ar impurities is unlikely to depend qualitatively on whether the 12 nearest neighbors of a typical lattice site include one Ar atom ($x = 0.09$), two Ar atoms ($x = 0.16$) or three Ar atoms ($x = 0.25$). Evidently the electrons are localized only by an Ar concentration of 0.25 or greater—i.e., in the glassy phase.

We have also found that the influence of orientational disorder on the transport of *neutral muonium atoms* is much the same as that on the electron: Mu is found to undergo localization in the $x = 0.25$ mixture [22] in the temperature range where it exhibits delocalized dynamics in pure solid nitrogen [23].

In conclusion, we have demonstrated a dramatic effect of orientational disorder on electron transport in an insulator. In contrast to electron *delocalization* in the orientationally ordered phase of α -N₂, electrons appear to be *localized* in the orientational glass (N₂)_{0.75}Ar_{0.25}. These mixtures may thus serve as model systems for studying electron localization in the absence of electron-electron interactions; our conclusions may be extended to other classes of insulating and semiconducting materials.

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- [1] N.F. Mott and E.A. Davis, *Electron Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1979).
- [2] P.W. Anderson, Phys. Rev. **109**, 1492 (1958).
- [3] P.A. Lee and T.V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).
- [4] N.F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1974).
- [5] U.T. Hochli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1990).
- [6] J.A. Hamida, E.B. Genio, and N.S. Sullivan, J. Low Temp. Phys. **103**, 49 (1996).
- [7] T.A. Scott, Phys. Rep. **27**, 89 (1976).
- [8] L.G. Ward, A.M. Saleh, and D.G. Haase, Phys. Rev. B **27**, 1832 (1983).
- [9] W. Press, B. Janik, and H. Grimm, Z. Phys. B **49**, 9 (1982).
- [10] H. Klee and K. Knorr, Phys. Rev. B **42**, 3152 (1990); **43**, 8658 (1991).
- [11] A. Schenck, *Muon Spin Rotation: Principles and Applications in Solid State Physics* (Adam Hilger, Bristol, 1986); S.F.J. Cox, J. Phys. C **20**, 3187 (1987); J.H. Brewer, in *Encyclopedia of Applied Physics*, edited by G.L. Trigg (VCH, New York, 1995).
- [12] E. Krasnoperov *et al.*, Phys. Rev. Lett. **69**, 1560 (1992).
- [13] V. Storchak, J.H. Brewer, and G.D. Morris, Phys. Lett. A **193**, 199 (1994).
- [14] V. Storchak, J.H. Brewer, and G.D. Morris, Phys. Rev. Lett. **75**, 2384 (1995).
- [15] V. Storchak *et al.*, Phys. Rev. B **59**, 10559 (1999).
- [16] V. Storchak, J.H. Brewer, and G.D. Morris, Phys. Rev. Lett. **76**, 2969 (1996).
- [17] V.G. Storchak, J.H. Brewer, and D.G. Eshchenko, Appl. Magn. Reson. **13**, 15 (1997).
- [18] V.G. Storchak *et al.*, Phys. Rev. Lett. **78**, 2835 (1997).
- [19] D.G. Eshchenko, V.G. Storchak, and G.D. Morris, Phys. Lett. A **264**, 226 (1999).
- [20] V.G. Storchak and N.V. Prokof'ev, Rev. Mod. Phys. **70**, 929 (1998).
- [21] *Cryocrystals*, edited by B.I. Verkin and A.F. Prikhotko (Naukova Dumka, Kiev, 1983).
- [22] V.G. Storchak *et al.*, Physica (Amsterdam) (to be published).
- [23] V. Storchak *et al.*, Phys. Rev. Lett. **72**, 3056 (1994).