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Electron Delocalization in α-Nitrogen

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Abstract

A new technique has been developed for measuring electron drift mobility in crystals on a microscopic scale through its effect on muonium ($Mu = \mu^+ + e^-$) atom formation *via* transport of electrons to thermalized positive muons (μ^+). Electron transport mechanisms are shown to be fundamentally different in the α and β phases of solid nitrogen, giving of about 5 orders of magnitude difference in electron mobilities. Contrary to previously reported results of macroscopic time-of-flight measurements, excess electrons appear to be delocalized in α-N_2.

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Molecular cryocrystals formed by diatomic molecules (solid H_2, N_2, O_2, CO, *etc.*) are the simplest molecular solids. Many peculiarities of these solids are connected with their molecules' rotational motion, which in fact determines many of the thermodynamic, kinetic and spectroscopic properties of molecular cryocrystals — in particular the existence of phase transitions in the solid state [1]. X-ray studies as well as specific heat and thermal expansion measurements show that phase transitions in these solids are accompanied by orientational ordering of molecules due to an anisotropic intermolecular interaction. Solid nitrogen (s-N_2) has two structural phases: in α-N_2 (below the transition temperature $T_{\alpha\beta} = 35.6$ K) the N_2 molecules are frozen along the diagonals of *fcc* unit cells, whereas in β-N_2 (above $T_{\alpha\beta}$) the molecules are free to rotate, forming an orientationally disordered crystal.

The relative simplicity of molecular cryocrystals makes them convenient testing grounds for theoretical models of the crystalline state, especially those addressing the transport properties of excess particles. Considerable progress has recently been made in understanding the transport of *neutral* particles in these solids [2–4]. However, the transport properties of *charged* particles in molecular cryocrystals have so far received relatively little attention and all the previous work [5–7] focused mainly on the *high temperature* phases of diatomic molecular cryocrystals. The mechanism of *electron* transport in molecular cryocrystals may be expected to be particularly interesting, given the remarkable transport properties of *atomic* cryocrystals (solid Ne, Ar, Kr and Xe), in which excess electrons were found to be *delocalized* [8]. (See also the review paper [9] and references therein).

Spectroscopic measurements and band structure calculations (see, for example, [1] and references therein) indicate that molecular cryocrystals possess very large energy gaps ($E_g \sim 10$ eV), so that even near the triple point the density of thermally activated carriers is extremely low. Experimental studies of charge transport in these insulators therefore require that excess carriers be generated in the crystal — for instance, through ionization of molecules by highly energetic particles such as electrons, α particles, photons *etc.*

Measurements of drift mobility by time-of-flight (TOF) techniques (see, for example, [10,9,5–7]) represent a very direct approach to the study of charge transport properties in solids. It should be noted, however, that in such experiments the path length between electrodes is *macroscopic*, making the results highly susceptible to spurious TOF changes if electrons interact with crystalline defects such as impurities, crystals strains and microcracks.

In this paper we demonstrate the use of muon spin rotation ($\mu\mathcal{SR}$) techniques [11] to avoid these difficulties by measuring the motion of electrons over much shorter distances. In $\mu^+\mathcal{SR}$ a large number ($\sim 10^7$) of 4 MeV μ^+ (positively charged muons) are stopped in the sample one at a time. Each incoming muon leaves behind an ionization track of excess electrons and ions liberated during the μ^+ thermalization process. Recent $\mu^+\mathcal{SR}$ experiments on s-N_2 [12] have shown that the spatial distribution of the ionization track products is highly anisotropic with respect to the final position of the muon: the μ^+ thermalizes well "downstream" from the end of its track. Some of the excess electrons generated in said track are mobile enough to reach the thermalized

muon and form the hydrogen-like muonium (Mu) atom with the μ^+ as its nucleus.

This scenario of *delayed* Mu formation [13] is logically distinguished from *prompt* Mu formation processes [14,15] by the muon energy involved. The latter are known to occur *epithermally* through cyclic charge exchange and are therefore essentially temperature independent. The former process involves *thermalized* particles and is crucially dependent on *electron mobility* (or, in some cases, muon mobility [16]); it can therefore be strongly temperature dependent. It has been shown that in solid nitrogen at least half the Mu fraction is delayed and the probability of delayed Mu formation has the same temperature dependence as the electron mobility [12].

In a weak transverse magnetic field (wTF) the characteristic Larmor precession frequency ω_{Mu} of (paramagnetic) Mu atoms is two orders of magnitude faster than, and in the opposite sense from, the Larmor frequency ω_μ of the bare μ^+ or any other diamagnetic species incorporating the muon: $\omega_{Mu} \approx -103\,\omega_\mu$, where $\omega_\mu = \gamma_\mu H$ and H is the magnetic field, with $\gamma_\mu = 2\pi \times 0.01355$ MHz/G. This allows unambiguous and quantitative identification of the fraction of muons forming Mu atoms at early times. It also permits a determination of the *time scale* of that formation by varying H, since Mu atoms which form (and begin precessing at ω_{Mu}) at different times will be out of phase with each other by an amount proportional to H. The present experiment exploits this technique.

Excess electrons are usually much more mobile than positive ions in a solid [5,9]; in s-N_2, for example, the diamagnetic state of positive muons has been shown to be static $N_2\mu^+$ molecular ions [17]. Therefore, Mu formation *via* convergence of muons and electrons is thought to be due to electron transport to the muon rather than *vice versa*. This circumstance permits development of a new technique for studying electron transport in matter: the electron mobility b_e in a crystal can be determined whenever the mean initial muon-electron distance R and the characteristic Mu formation time τ can be simultaneously measured in delayed Mu formation.

In different insulators, electron transport is determined by qualitatively different interactions of electrons with the medium. Measurements on Ar, Kr and Xe crystals [8] show clearly that electron mobilities in these solids are comparable to those found in wide-band semiconductors ($b_e \sim 10^3$ cm^{2}sec^{-1}V^{-1}), which encouraged different authors to apply Shockley's well-known theory [18] originally developed for semiconducting Ge. An approximation in which the free charge carriers are completely delocalized and the electron-phonon interaction is treated as a perturbation gave an adequate description of the observed electron transport. A nonlinear dependence of the electron drift velocity on electric field was explained by "heating up" of a Maxwellian electron velocity distribution. A more general electron transport theory [19] is based on Shockley's approach but also takes into account the structure of the medium containing the electrons. These theories' good agreement with experiments gives one confidence that the description in terms of quasi-free band propagation of electrons is also valid in rare gas solids.

The rather low electron mobilities found in the diatomic solids of N_2, CO and O_2 [5] ($b_e \sim 10^{-2} - 10^{-3}$ cm^{2}sec^{-1}V^{-1}) and H_2 [6,7] ($b_e \sim 10^{-5}$ cm^{2}sec^{-1}V^{-1}) suggest that a fundamentally different mechanism of electron transport occurs in these materials.

The *localization* of excess electrons due to strong interactions with excitations of the medium was proposed to explain such low values of drift mobility. Formation of a small polaron [20] rather than an electron bubble [21] was suggested to be the case in solid nitrogen. The well known small polaron theory [20] has successfully described low mobility electron transport in diatomic solids [5].

The transition from β-N_2 to α-N_2 in solid nitrogen was accompanied by a comparatively sharp increase in electron mobility [5]. However, the measured values of electron mobility in α-N_2 were reported to be of the same order of magnitude as those in β-N_2, suggesting the same mechanism of electron localization.

In this paper we present unambiguous evidence that electron transport mechanisms are in fact qualitatively different in the α and β phases of solid nitrogen. Our μ^+SR measurements reveal an enormous increase in electron mobility in α-N_2, suggesting an onset of band-like propagation.

The present experiments were performed on the M15 and M13 surface muon beam lines at TRIUMF. Ultra high purity nitrogen ($^{14}N_2$ with $\sim 10^{-5}$ impurity content) was used to grow perfectly transparent crystals at a speed of about 4 mm/hour. An external electric field of up to 8 kV/cm was generated by applying high voltage to two parallel grids of very fine wires located in front of and behind the sample cell. Positive muons of 28 MeV/c momentum and 100% spin polarization were stopped in the crystals of solid N_2 and wTF-μ^+SR measurements were made in various electric and magnetic fields.

Both muonium (Mu) and diamagnetic (D) signals were evident in solid N_2 at all temperatures. Therefore the overall muon decay asymmetry was described by

$$A(t) = A_{\rm Mu} e^{-\lambda_{\rm Mu} t} \cos(\omega_{\rm Mu} t + \varphi) + A_D e^{-\lambda_D t} \cos \omega_\mu t \,, \qquad (1)$$

where $A_{\rm Mu}$ and A_D are respectively the muonium and diamagnetic amplitudes (muon decay asymmetries), $\lambda_{\rm Mu}$ and λ_D are the corresponding relaxation rates and φ is the apparent initial phase of the Mu precession signal.

Figure 1 shows typical wTF-μ^+SR time spectra in solid α-N_2 at 20 K, binned coarsely to show only the D component, at three different electric fields (E); the E-dependence of the diamagnetic amplitude is shown along with that of the Mu signal in Fig. 2. The strong electric field dependence of both components confirms that delayed Mu formation takes place in s-N_2.

The characteristic muon-electron distance R in α-N_2 was determined by measurements of this E-dependence. A positive sign for E specifies that the electric field is applied parallel to the initial μ^+ momentum direction, thus pulling the μ^+ and e^- apart and giving rise to an increased D amplitude. Negative E denotes the situation where the electric field is antiparallel to the initial μ^+ momentum, thus pushing the μ^+ and e^- together to enhance the probability of Mu formation. As expected, $A_{\rm Mu}$ changes by about half as much as A_D. This is because the amplitude of the Mu signal represents only that half of the muonium ensemble which is formed with electron and muon spins parallel; in the other half the muon polarization oscillates at a frequency which is too high to be observed in conventional wTF experiments [11].

The E-dependences shown in Fig. 2 also demonstrate a strong anisotropy in the muon-electron spatial distribution in solid nitrogen: muons are thermalized downstream

(*i.e.* in the direction of the initial muon momentum) from the last radiolysis electrons of the muon's ionization track. The small reduction of the Mu amplitude by $|\vec{E}| > 5$ kV/cm in the negative direction suggests a compensation of the Coulomb attraction between μ^+ and e^- by the external electric field, which in turn provides an estimate of $R \approx 5 \times 10^{-6}$ cm for the $\mu^+ - e^-$ distance in α-N_2 from the relation $E = e/\epsilon R^2$, where $\epsilon = 1.45$ is the dielectric constant of s-N_2 and e is the electron charge. Since the typical $\mu^+ - e^-$ distance is expected to depend so weakly on E ($R \propto E^{-1/2}$), we believe that our value is a reasonably reliable estimate.

Analogous measurements in β-N_2 at $T = 59$ K revealed a much weaker electric field dependence, giving an estimate of the characteristic $\mu^+ - e^-$ distance about half that in α-N_2.

The Mu formation time τ (*i.e.* the characteristic time for e^- transport to the μ^+) can be determined by measurement of the magnetic field dependence of the Mu amplitude. Assuming that the muonium formation process is governed by a first-order kinetic equation $dn_{Mu}(t) = -dn_\mu(t) = \lambda n_\mu(t)dt$, where $\lambda \equiv 1/\tau$ is the characteristic formation rate, the muonium amplitude has been shown [13] to be

$$A_{Mu} \propto \frac{\lambda}{\sqrt{\lambda^2 + \omega_{Mu}^2}} . \tag{2}$$

The assumption of a constant rate of arrival of the e^- at the μ^+ cannot be strictly valid, of course; nevertheless Eq. (2) should give a reasonable estimate for the parameter λ. This parameter determines the average time $\tau \equiv \lambda^{-1}$ needed for the electron to drift to the muon. Equation (2) clearly reflects the phenomenon of delayed muonium formation: different Mu atoms are formed at different times and the phase coherence among the precessing Mu atoms is lost. The higher the magnetic field, the stronger the effect of dephasing which results in the reduction of the Mu amplitude.

In low electric fields, electron mobility is independent of E and the definition of the charge mobility gives an expression for the Mu formation time

$$\tau \equiv \lambda^{-1} = \frac{R^3 \epsilon}{3eb_e} . \tag{3}$$

Certainly, at short distances where the electric field due to the muon charge is large, the electron mobility is no longer constant. However, it can be argued that Eq. (3) is still a good approximation because the recombination time is determined mainly by slow motion at large distances in low electric fields. Expressions (2) and (3) allow one to extract the electron mobility b_e from the magnetic field dependence of A_{Mu} provided R is known from the electric field dependence of A_D and A_{Mu}.

Figure 3 shows the magnetic field dependence of A_{Mu} in α-N_2 (circles) and in β-N_2 (stars). The solid curves show numerical calculations according to Eqs. (2) and (3) with the values of electron mobility determined from TOF measurements [5]. In β-N_2 both μ^+SR and TOF techniques give the same value for the electron drift mobility. In α-N_2, however, A_{Mu} turns out to be field independent (*i.e.* $\lambda \gg \omega_{Mu}$), which means

that the Mu formation time is much shorter (*i.e.* the electron mobility is several orders of magnitude higher) than expected from TOF measurements.

It is known that solid nitrogen undergoes a huge volume jump (about 1%) at the α-β transition [1]. Such a big change in crystal volume inevitably creates strong thermal strains and leads to many small cracks in the crystal. Direct optical examination in reflected light did reveal a tendency of solid N_2 to develop cracks at α-β transition [1]. Probably cracking of the crystal at the α-β transition hampered measurements of electron mobility at low temperatures using the TOF technique [5], which relies on electron drift over the *macroscopic* distances between electrodes (typically about 10^{-2} cm). We claim that the μ^+SR technique, which involves *microscopic* characteristic distances ($\sim 10^{-6}$ to 10^{-5} cm), avoids these difficulties.

Such a high value of electron mobility suggests that the electron transport mechanism in α-N_2 is fundamentally different from that in β-N_2. Probably the *localization* of electrons *does not occur* in α-N_2 and Shockley's delocalized approximation [18] can be applied. Additional support for this assumption comes from the form of the electric field dependence of A_{Mu} and A_D. In the simplified approach both A_{Mu} and A_D should be proportional to the electron drift velocity. According to Shockley's theory, at high enough electric field the mean electron drift velocity deviates from its linear dependence on E due to "heating up" of the electron velocity distribution, producing a $\sqrt{E}$ dependence instead. The same peculiarity is seen in Fig. 3. The approximate value of the electron mobility in α-N_2 can be extracted by taking into account that the onset of this nonlinear deviation takes place when the electron drift velocity $v \simeq 1.5u$, where u is the velocity of sound [18]. The deviation of $A_{\mathrm{Mu}}(E)$ and $A_D(E)$ from a linear E-dependence occurs at about $E_c \approx 2$ kV/cm. The velocity of sound in solid nitrogen has been measured to be $u = 1.8 \times 10^5$ cm/s at $T = 20$ K [22]. Therefore, our μ^+SR measurements imply $b_e \approx 10^2$ cm^{2}s^{-1}V^{-1} in α-N_2 at $T = 20$ K. This value is about 5 orders of magnitude higher than that extracted from TOF measurements in α-N_2 at 30 K [5]. It differs by more than 5 orders of magnitude from the electron mobility in β-N_2, which strongly supports our conclusion that excess electrons are delocalized in α-N_2. This in turn suggests that a possible mechanism for electron localization in β-N_2 may be interactions with the rotational modes of N_2 molecules — a scattering mechanism that is absent in α-N_2 due to the orientational ordering of the molecules.

In conclusion, we have demonstrated a new technique for measuring the drift mobility of charged particles on a microscopic scale. The electron transport mechanisms are shown to be fundamentally different in the α and β phases of solid nitrogen, probably due to the rotational ordering at low temperatures. We conclude that electrons are probably delocalized in α-N_2.

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FIGURE CAPTIONS

Fig. 1. Diamagnetic precession signals in s-N_2 at 20 K in a transverse magnetic field of 35 Oe, for several electric fields E: (a) $E = +7.54$ kV/cm; (b) $E = 0$; (c) $E = -2$ kV/cm. The muonium signal is averaged to zero by adjusting the binning width to a large integer multiple of the Mu precession period.

Fig. 2. Electric field dependences of muonium (Mu, circles) and diamagnetic (D, stars) amplitudes (muon decay asymmetries) in α-N_2 at $T = 20$ K. The change in A_D is about twice that in A_{Mu}.

Fig. 3. Experimental magnetic field dependences of muonium amplitudes in α-N_2 at $T = 20$ K (circles) and in β-N_2 at $T = 59$ K (stars). Smooth curves represent numerical calculations using values of electron drift mobility from [5] (*localized* electron model).

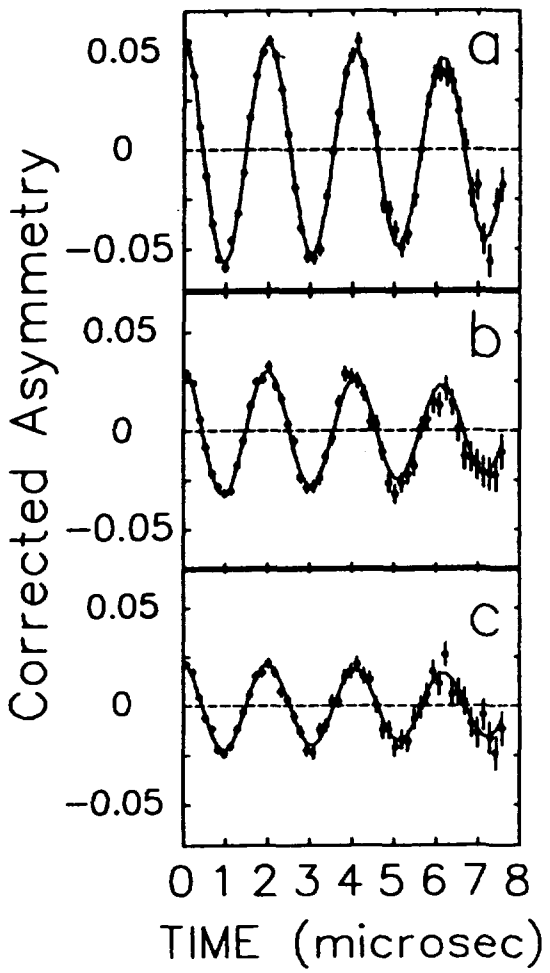

Fig. 1

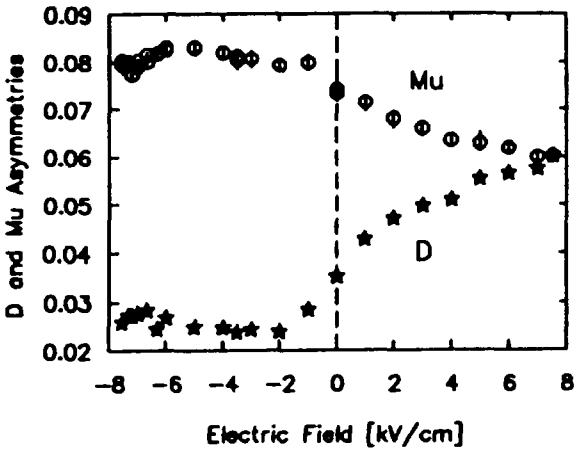

Fig. 2

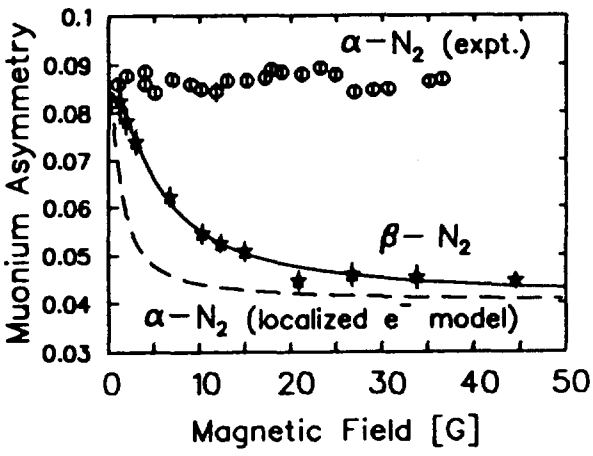

Fig. 3