Fast and Slow Electrons in Liquid Neon

V. Storchak
Kurchatov Institute, Kurchatov Sq. 1, Moscow 123182, Russia

J. H. Brewer and G. D. Morris
Canadian Institute for Advanced Research and Department of Physics, University of British Columbia,
Vancouver, British Columbia, Canada V6T 2A3
(Received 11 January 1996)

Muon spin relaxation measurements in liquid neon in electric fields up to 35 kV/cm reveal two types of radiolysis electrons created in the positive muon's ionization track. Some of these electrons are initially delocalized (fast) and reach the μ^+ to form a muonium atom *before* they can become localized (slow) inside bubbles. Fast and slow electrons have similar initial spatial distributions relative to the thermalized muon.

PACS numbers: 73.20.Jc, 66.30.Jt, 67.80.Mg, 76.75.+i

Transport of excess carriers in insulators is a topic of major importance in condensed matter physics. While electronic conduction in crystalline insulators has (understandably) enjoyed intense interest for many decades, the investigation of disordered media—in particular, liquids—has only recently attracted similar attention. The simplest class of liquids is the liquefied rare gases (He, Ne, Ar, Kr, Xe) which in the pure states are ideal insulators: they are comprised of atoms with ionization potentials of more than 10 eV, and their conduction bands are well separated from their valence electron levels by a large forbidden gap. This property allows the injection and observation of arbitrarily small concentrations of charge carriers, the study of which should produce a deeper understanding of electronic charge carrier transport in liquids and other disordered systems.

Another reason for the increasing interest in electronic conduction in rare gas liquids (RGL) is their employment in high energy physics experiments as working media for ionization chambers and other particle detection systems.

A remarkable feature of the heavy RGL (Ar, Kr, and Xe) is their similarity to liquid metals and semiconductors [1]. The heavy rare gas *solids* (RGS) have electron mobilities b comparable to those of conventional semiconductors ($\sim 10^3$ cm^2 V^{-1} s^{-1}), implying the existence of extended delocalized electron states (band states) [1,2]. One might expect a dramatic reduction of b to accompany the disappearance of translational symmetry upon melting. On the contrary, experiments in heavy RGL [2] indicate that b only decreases by a factor of 2 upon melting. Many perfect metals and semiconductors exhibit the same factor of 2 decrease in conductivity upon melting. This fact may imply the existence of a band of extended electron states in *liquids* (including insulators).

In the light RGL (He and Ne) the mobility of excess electrons was found to be some 5 orders of magnitude lower than in the heavy RGL (about 0.025 cm^2 V^{-1} s^{-1} at 4.2 K in He and 0.0016 cm^2 V^{-1} s^{-1} at 25 K in Ne) [3–5]. Such a dramatic difference in electron mobility between light and heavy RGL has been interpreted [1] as arising from electron *localization* in a "bubble" in the former, contrasted with quasifree propagation of *delocalized* electrons in the latter.

Such bubbles form because of the Pauli exclusion principle: a space is opened up around the excess electron by a strong short-range repulsive exchange interaction between it and the electrons of host atoms. Once the excess electron is thus localized, its zero-point kinetic energy tends to expand the resultant bubble, while weak long-range attractive interactions (caused by the polarizability of host atoms) tend to contract it, assisted by pressure-volume and surface energies. In liquid He the repulsive part of the interaction is strong while (due to a low polarizability) the attractive part is weak, leading to formation of a stable bubble with a radius of about 10–20 Å [6]. Polarizability increases with increasing atomic number until in liquid Ar, Kr, and Xe its attractive contribution overcomes the repulsive part of the interaction. Therefore electron localization in a bubble *does not occur* in heavy RGL.

Liquid neon (ℓ-Ne) represents a borderline case where the strength of the repulsive exchange interaction turns out to be very close to that of the attractive interactions which contract the bubble. Calculations using the bubble stability criterion [6] showed that in ℓ-Ne one could not make definite predictions based on theory because of the approximations made. However, time-of-flight (TOF) experiments [4,5] revealed only low mobility negative carriers in ℓ-Ne which were identified as stable electronic bubbles. Until now, no high mobility electrons have been found in ℓ-Ne.

In this paper we report the first direct observation of a high mobility electron state in ℓ-Ne. We believe this state to be a delocalized quasifree carrier.

Recent μSR (muon spin rotation [7]) experiments in solid nitrogen [8] have introduced a novel technique for measuring electron drift mobility in cases where TOF methods are confounded by crystalline defects such as thermal stress fractures, which interfere with charge transport over the required macroscopic distances (typically $>10^{-2}$ cm). The new technique utilizes the delayed formation of muonium ($\mathrm{Mu} = \mu^+ + e^-$) atoms [9] via transport of electrons to thermalized positive muons (μ^+) over distances of 10^{-6}–10^{-4} cm, the average separation between the μ^+ and the last free electron liberated during its thermalization process. Previous μSR experiments in liquid helium [10], solid and liquid nitrogen [8,9], solid neon [11], and solid and liquid neon and argon [12] have shown that the spatial distribution of the ionization track products is highly anisotropic with respect to the final position of the muon: in liquid He, solid N_2, and solid Ne the μ^+ thermalizes well "downstream" from the center of the spatial distribution of the last excess electrons generated in the μ^+ track. Some of the excess electrons are mobile enough to reach the thermalized muon and form a muonium atom. The new technique [8] is based on measurements of the *time scale* for this process, which depends critically upon the electron mobility.

The first μSR experiment in condensed Ne [13] revealed a large signal at the characteristic frequency of muonium precession, $\omega_{\mathrm{Mu}} \approx -103\omega_\mu$, where $\omega_\mu = \gamma_\mu H$ is the Larmor frequency of the bare muon, H is the external transverse magnetic field, and $\gamma_\mu = 2\pi \times 0.013\,55$ MHz/G. The fact that Mu is formed with high probability in both solid and liquid neon may seem surprising in view of the fact that the Ne ionization potential ($\approx$21 eV) greatly exceeds that of Mu ($\approx$13.5 eV) and the fact that *no* Mu signal is observed in *gaseous* Ne [14]. However, this circumstance makes perfect sense if one assumes that Mu formation in condensed media is governed predominantly by the capture of a mobile electron by the thermalized μ^+. The muonium signal in solid Ne was found experimentally [13] to account for about 85% of the incoming muons; this Mu fraction decreases sharply to about 25% in liquid Ne. The reduction of the Mu fraction by a factor of 4 upon melting has been interpreted [11] as the result of a dramatic (more than 5 orders of magnitude) change in electron mobility from about 600 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in solid Ne to about 0.0016 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$ in liquid Ne [1]. In this picture, all or most of the 25% Mu fraction in liquid Ne would have to be the result of "prompt" [9] *epithermal* Mu formation *during* μ^+ thermalization. This hypothesis, however, contradicts the complete absence of Mu formation in gaseous Ne [14]. We propose a different interpretation: namely, that *some* of the excess electrons liberated in the muon track *avoid localization* (bubble formation) long enough to find their way to the thermalized μ^+ and form muonium.

Those electrons which *do* form bubbles will *also* be captured by the μ^+ and form Mu, albeit at very much later times. *These are also observed* in the present experiment, and the effect of applied electric field on their capture by the μ^+ is *virtually identical to that of the "fast" delocalized electrons* (see below), demonstrating that both have the same initial spatial distribution with respect to the muon and, in fact, arise from the same processes.

As far as the authors know, there has not yet been any experimental measurement of the characteristic bubble formation time τ_b in liquid He or Ne. One can argue that τ_b might be estimated by simply dividing the characteristic bubble dimension (about 6–7 Å in liquid Ne [5]) by the velocity of sound. It is not surprising that this estimate gives a τ_b of the same order of magnitude as the inverse Debye frequency (about 10^{-13}–10^{-12} s).

In this paper we present experimental evidence that Mu formation in liquid neon takes place at thermal energies via the delayed channel, namely, transport of *delocalized* electrons to positive muons. Localization of such electrons in bubbles does not occur within less than approximately 10^{-9} s.

The present experiments were performed on the M20 surface muon beam line at TRIUMF. Ultrahigh purity neon gas ($\sim 10^{-5}$ impurity content, the same as in [13]) was condensed into the sample cell, and positive muons of 28 MeV/c momentum and 100% spin polarization were stopped in the sample. Transverse magnetic field muon spin rotation–relaxation (TF-μ^+SR) measurements were then made in various applied electric and magnetic fields.

In liquid neon, most of the muon polarization (about 70%) is manifest in the diamagnetic signal (muon precession at ω_μ), which consists of two distinct components, slow relaxing (S) and fast relaxing (F). A smaller signal arises from muonium precession at two frequencies, ω_{12} and ω_{23}, whose average is ω_{Mu} and whose difference is given by $\omega_{23} - \omega_{12} \approx 2\omega_{\mathrm{Mu}}^2/\omega_0$, where ω_0 is the muonium hyperfine frequency, which is found to be $\omega_0 = 4382(9)$ MHz in ℓ-Ne, 1.8(2)% smaller than the vacuum value of 4463 MHz. The overall time dependence of the μ^+ polarization at 51 G was therefore described by the following expression:

$$\begin{aligned} A_0 P(t) = {} & \frac{A_{\mathrm{Mu}}}{2} \exp(-\lambda_{\mathrm{Mu}} t) \\ & \times [\cos(\omega_{12} t + \varphi) + \cos(\omega_{23} t + \varphi)] \\ & + [A_F \exp(-\lambda_F t) + A_S \exp(-\lambda_S t)] \cos\omega_\mu t\,, \end{aligned} \tag{1}$$

where A_0 is a normalization factor (the maximum muon decay asymmetry); A_{Mu}, A_F, and A_S are muonium, fast-relaxing diamagnetic, and slow-relaxing diamagnetic asymmetries (proportional to the corresponding fractions); and λ_{Mu}, λ_F, and λ_S are the corresponding relaxation rates. Typical TF-μ^+SR spectra for the muonium component in ℓ-Ne at 24.9 K are shown in Fig. 1 for different external electric fields.

Figure 2 shows the electric field dependences of the net (S plus F) diamagnetic (stars) and muonium (circles) amplitudes. Positive and negative E correspond, respectively,

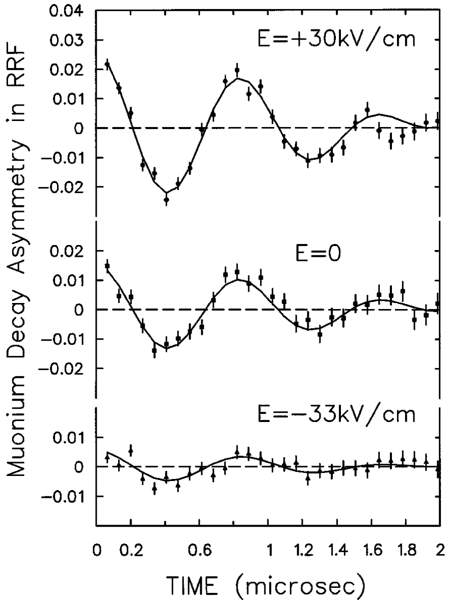

FIG. 1. Muonium precession signals in ℓ-Ne at $T = 24.9$ K in a transverse magnetic field of 51 G at several electric fields E [(a) $E = +33.3$ kV/cm, (b) $E = 0$, and (c) $E = -30$ kV/cm]. The data are shown in the rotating reference frame at a frequency just below that of Mu precession. There is a node around 2 μs due to "beats" caused by the hyperfine splitting of Mu precession in 51 G; this is *not* the result of Mu relaxation.

to the external electric field applied parallel and antiparallel to the initial μ^+ momentum direction; thus positive E pulls the μ^+ and e^- apart, increasing the diamagnetic amplitude, whereas negative E pushes them together to help form Mu atoms. Large positive electric field almost completely quenches Mu formation, which indicates that almost all Mu is formed via the delayed channel.

The E dependences shown in Fig. 2 also reveal a strong anisotropy in the spatial distribution of the muons relative to the last electrons produced in their ionization tracks in ℓ-Ne: muons thermalize "downstream" of their radiolysis electrons (i.e., in the direction of the initial muon momentum). An analogous anisotropic muon-electron spatial distribution was found in solid α-nitrogen [8,9].

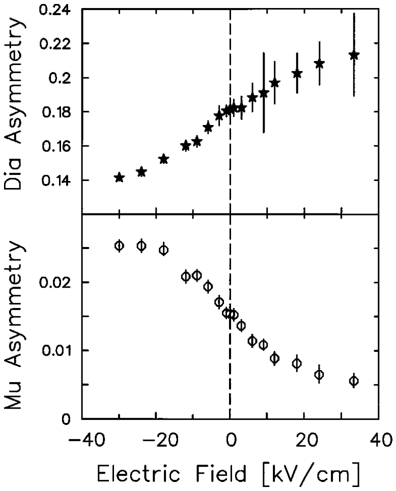

FIG. 2. Electric field dependences of Mu (circles) and diamagnetic (stars) amplitudes in ℓ-Ne at $T = 24.9$ K.

Above about $E_0 \approx 25 \pm 5$ kV/cm, the muonium and diamagnetic amplitudes level off, suggesting that this is the field required to compensate the average Coulomb interaction between the muon and electron. This in turn provides an estimate of the characteristic muon-electron distance R in ℓ-Ne from the relation $E_0 = e/\epsilon R^2$, where $\epsilon = 1.2$ is the dielectric constant. The result is $R = (2.2 \pm 0.2) \times 10^{-6}$ cm, about 1.5 times smaller than the characteristic muon-electron distances found in liquid nitrogen [9] and about half that in solid α-nitrogen [8] or solid Ne [11,12].

If one assumes that *all* electrons are *localized* in bubbles, as stated in [4] and [5], then these localized charges would move as *polarons* in low electric fields with a drift velocity v proportional to the applied electric field: $v = bE$, where b is the charge mobility. In this case the muonium formation time could be estimated [8] to be

$$\tau \approx R^3/3bE\,, \qquad (2)$$

where $b = b_- + b_+$ is the net mobility of negative (b_-) and positive (b_+) charges. Drift mobilities of positive and negative localized charge carriers in ℓ-Ne were both determined to be about 1.5×10^{-3} cm^2 s^{-1} V^{-1} at 25 K [5]. Using the value of R determined above, we can thus estimate the characteristic muonium formation time in ℓ-Ne via *localized* charge transport to be about 10^{-8} s.

The average Larmor frequency of Mu precession in a magnetic field of $H = 51$ G is $\omega_{\mathrm{Mu}} = 2\pi H\gamma_{\mathrm{Mu}} = 0.45 \times 10^9$ s^{-1}, where $\gamma_{\mathrm{Mu}} = 1.3945$ MHz/G is the muonium magnetogyric ratio. Unless the criterion

$$\omega_{\mathrm{Mu}}\tau \ll 1 \qquad (3)$$

is satisfied [8], coherence among Mu atoms formed at different times will be lost and the amplitude of the Mu precession signal must be drastically reduced. For the *localized* electron model described above, $\omega_{\mathrm{Mu}}\tau \approx 4.5$ and there should be *no* muonium signal observed in ℓ-Ne. Since this is emphatically not the case—a large amplitude, E-dependent Mu precession signal is clearly evident—we may conclude that condition (3) is well satisfied and the muonium formation time is much less than that estimated in the framework of the *localized* charge transport model. This in turn implies a much higher electron mobility, consistent with Mu formation in ℓ-Ne due primarily to transport of *delocalized* electrons to positive muons.

We conclude that the electrons that reach the μ^+ to form muonium cannot become localized in bubbles in times less than about 10^{-9} s. However, there is also evidence for another component that reaches the μ^+ on a time scale 3–4 orders of magnitude slower than the delocalized electrons: the *diamagnetic* signal (from muons which have

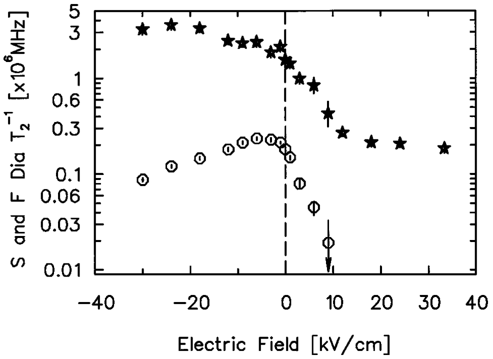

FIG. 3. Electric field dependences of relaxation rates of fast (stars) and slow (circles) diamagnetic components in ℓ-Ne at $T = 24.9$ K.

not yet formed muonium) presents two components, one relaxing very slowly and the other relaxing much more rapidly. Both components exhibit a strong electric field dependence, as shown in Fig. 3.

The most probable reason for the relaxation of the diamagnetic signal is the slow arrival of negative polarons at the μ^+, resulting in *very* delayed Mu formation. Criterion (3) is not satisfied for this Mu fraction, so it cannot be seen in the current experiment. The "very delayed" electrons responsible for this fraction cannot just be initially further away from the muon, since that would make them far more susceptible to electric field; instead, they respond to E almost the same as do *delocalized* electrons, implying that they are typically the same distance away from the muon. (It is this distance, not the electron's mobility or effective mass, that determines the electric field exerted by the muon, which E must overcome to influence delayed Mu formation.)

The depolarization rates of the two diamagnetic components [recall Eq. (1)] differ by more than an order of magnitude at negative electric fields. (At positive electric fields of more than about 5 kV/cm it becomes difficult to distinguish the two components.) Two different time scales for diamagnetic relaxation suggest two different kind of *polarons*. One obvious candidate is, of course, electrons localized in bubbles [4,5] moving according to a viscosity mechanism.

Our results for the diamagnetic signal(s) are consistent with formation of bubbles and/or some other type of slow-moving polarons by radiolysis electrons on a time scale short compared to $\sim 10^{-9}$ s. These electrons migrate to the μ^+ and form Mu atoms on a very slow time scale consistent with the low mobility predicted for such polarons. They show the same sensitivity to electric field as the fast component due to delocalized electrons and are therefore found in the same initial spatial distribution relative to the stopped μ^+.

We have also conclusively demonstrated the presence of *delocalized* electrons in ℓ-Ne at 24.9 K; a substantial fraction of these electrons survive localization long enough to traverse the typical distance of $\sim 2 \times 10^{-6}$ cm to the μ^+ where they form Mu in times short compared to the Mu Larmor precession period (2.2 ns in this experiment). The nature of the differentiation of the excess electrons into *localized* and *delocalized* species is not yet understood; we do not know if these two kinds of charge carriers *coexist* in ℓ-Ne for times long compared to the polaron formation time, or if there is simply a *competition* between Mu formation and polaron formation for the initially delocalized electrons.

This work was supported by the Canadian Institute for Advanced Research, the Natural Sciences and Engineering Research Council, and (through TRIUMF) the National Research Council of Canada. One of us (V. S.) was also supported by the International Science Foundation, the INTAS Foundation and the Royal Society of the United Kingdom. We would like to thank N. V. Prokof'ev for useful discussions and C. Ballard and M. Good for technical support.

[1] W. E. Spear and P. G. Le Comber, in *Rare Gas Solids,* edited by M. L. Klein and J. A. Venables (Academic Press, New York, 1977), p. 1120.
[2] L. S. Miller, S. Howe, and W. E. Spear, Phys. Rev. **166**, 871 (1968).
[3] L. Meyer *et al.,* Phys. Rev. **126**, 1927 (1962).
[4] L. Bruschi *et al.,* Phys. Rev. Lett. **28**, 1504 (1972).
[5] R. J. Loveland *et al.,* Phys. Lett. **39A**, 225 (1972).
[6] B. E. Springett *et al.,* J. Chem. Phys. **48**, 2720 (1968).
[7] 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* (VCH Publishers, New York, 1994), Vol. 11, p. 23.
[8] V. Storchak, J. H. Brewer, and G. D. Morris, Phys. Rev. Lett. **75**, 2384 (1995).
[9] V. Storchak, J. H. Brewer, and G. D. Morris, Phys. Lett. A **193**, 199 (1994).
[10] E. Krasnoperov *et al.,* Phys. Rev. Lett. **69**, 1560 (1992).
[11] E. Krasnoperov *et al.,* JETP Lett. **59**, 749 (1994).
[12] V. Storchak, J. H. Brewer, and G. D. Morris (to be published).
[13] V. Storchak *et al.,* Hyperfine Interactions **85**, 109 (1994).
[14] D. G. Fleming *et al.,* Chem. Phys. **82**, 75 (1983); D. J. Arseneau, Ph.D. thesis, University of British Columbia, 1992 (unpublished).