film-mass loading effect. Hence we expect our data points to extrapolate to a straight line of lower slope $d\sigma_n/dD = \rho_n$(bulk). As one can see from the figure, this is, in fact, the case. Using this notion one calculates a residual superfluid fraction of about $(75 \pm 3)\%$ whereas the tabulated vapor pressure bulk value is 80%. Considering the fact that the whole of the abscissa of Fig. 4 only spans about 30 atomic layers, we consider our results in remarkably good agreement with expectations and accept them as further evidence that we are indeed making direct measurements of the superfluid fraction in very thin films.

We wish to thank Dr. C. D. Stockbridge, Dr. William H. King, Jr., and Mr. D. R. Montgomery for some helpful discussions on the quartz microbalance. Credit goes to Mr. S. C. Choudhery for the original construction of the cryogenic adsorption probe and we wish to acknowledge useful discussions with Professor I. Rudnick.

---

*Work supported by a grant from the California Institute of Technology President's Fund.

[1] R. S. Kagiwada, J. C. Fraser, I. Rudnick, and D. Bergman, Phys. Rev. Lett. 22, 338 (1969).

[2] R. P. Henkel, G. Kukich, and J. D. Reppy, in *Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968,* edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (St. Andrews University Press, St. Andrews, Scotland, 1969).

[3] R. P. Henkel, E. N. Smith, and J. D. Reppy, Phys. Rev. Lett. 23, 1276 (1969).

[4] D. F. Brewer and K. Mendelssohn, Proc. Roy. Soc., Ser. A 260, 1 (1961).

[5] K. R. Atkins and I. Rudnick, in *Progress in Low Temperature Physics,* edited by C. J. Gorter (North-Holland, Amsterdam, 1970), Vol. VI, Chap. 2.

[6] J. B. Brown and M. G. Tong, in *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto, Japan, 1970,* edited by E. Kanda, (Keigaku Publishing Co., Tokyo, 1971), p. 113.

[7] C. D. Stockbridge, in *Vacuum Microbalance Techniques,* edited by K. H. Behrndt (Plenum, New York, 1966), Vol. 5, pp. 147–205.

[8] G. Sauerbrey, Z. Phys. 155, 206 (1959).

[9] Since we employ a Colpitt-Clapp type of oscillator circuit, the crystal operates in a parallel resonance mode shunted by approximately 20 pF and the resonant frequency of the ensemble is essentially the natural one of the quartz crystal itself.

[10] P. A. Simpson and A. H. Morgan, National Bureau of Standards Report No. 6080, 1959 (unpublished).

[11] J. P. Hobson, Can. J. Phys. 37, 300 (1959).

[12] R. Bowers, Phys. Rev. 91, 1016 (1953).

[13] D. F. Brewer and K. Mendelssohn, Proc. Roy. Soc., Ser. A 260, 1 (1961).

[14] D. M. Young and A. D. Crowell, *Physical Adsorption of Gases* (Butterworths, London, 1962).

[15] The value $\theta \simeq 87$°K has been employed in the work of Rudnick *et al.* [I. Rudnick, R. S. Kagiwada, J. C. Fraser, and E. Guyon, Phys. Rev. Lett. 20, 430 (1968)], but measurements of C. H. Anderson and E. S. Sabisky [Phys. Rev. Lett. 24, 1049 (1970)] yielded $\theta = 16$°K. Cf. also R. Bowers, Phil. Mag. 44, 485 (1953).

Positive Impurity Ions in He II†

Warren W. Johnson and William I. Glaberson*
Department of Physics, Rutgers, The State University, New Brunswick, New Jersey 08903

(Received 24 April 1972)

We have developed a technique for introducing a variety of impurity atomic ions into liquid helium and measuring their mobility. We find that, in contrast with predictions of the "snowball" model of Atkins, the ion mobility depends on the atomic number of the core ion in a way that cannot be explained simply in terms of the mass of the ion. The relative mobility of ^{40}Ca and ^{48}Ca ions has been measured and is consistent with existing theories.

For many years ions have served as useful tools in investigations involving liquid helium. The drag force encountered by an ion in motion through the superfluid exhibited the energy spectrum of the elementary excitations.[1] Ions have been used to generate quantized vortex rings,[2] and studies of the interactions between ions and vortex lines provided useful information about quantized vorticity.[3]

The nature of the ions themselves has been the subject of considerable research. The observation of the energy well seen by the electron in its bubble,[4] and the explanation of the low-temperature mobility in terms of resonant oscillations of the bubble surface,[5] have provided strong evidence for the correctness of the bubble model for

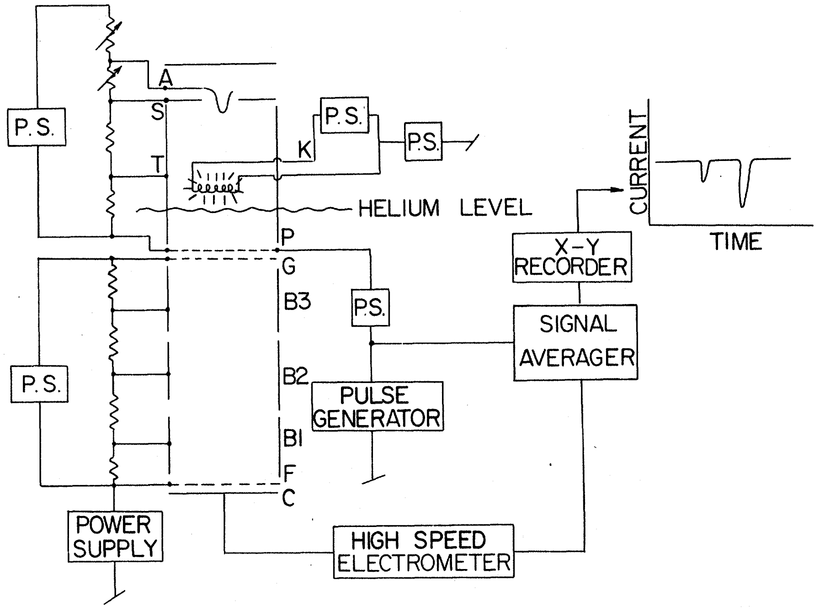

FIG. 1. Schematic diagram of the experimental cell and associated electronics.

the negative ion.[6] On the other hand, except for rough measurements of the size[7] and mass[8] of the ion, no detailed experimental verification exists of the snowball model of positive ions suggested by Atkins.[9] Ihas and Sanders[10] introduced positive potassium ions into superfluid helium and measured a mobility which was consistent with a mass-dependent mobility calculation of Bowley[11] based on the Atkins model. We have been able to introduce a wide variety of atomic ions into liquid helium, and our results indicate that consistency with the Atkins model is fortuitous for potassium and that other atomic ion data are inconsistent with the continuum snowball picture.

Our experimental procedure is illustrated in Fig. 1. A continuous electrical discharge is maintained in the helium vapor near the filament K. The filament is coated, prior to cooldown, with a solution or suspension of some compound containing the positive ion of interest. The filament is heated, introducing the compound into the discharge, and the appropriate ions are drawn through the helium surface by an electric field. The ions then enter a mobility cell, and simultaneous measurements of the helium and impurity ion mobility are made. Details of the experimental procedure will be published elsewhere.

A difficulty encountered in the experiments was the assignment of particular peaks in the current-versus-time data to the appropriate ions. Occasionally, extra impurity peaks appeared. These were attributed, on the basis of peak amplitude and occurrence in association with other ions, to trace impurities in the compound used, the filament itself, or other parts of the apparatus. Because of the experimental technique employed, care was taken to ensure that the mobilities measured were associated with the atomic rather than with the compound molecular ion. This was accomplished by repeating the experiments with a variety of molecules associated with the same positive ion and observing the same peak. In the case of barium, for example, the compounds $BaCl_2$, $BaBr_2$, $Ba(NO_3)_2$, BaO, $Ba(OH)_2$, and $BaSO_4$, differing widely in mass and shape, provided identical ion peak positions.

Some of our measured relative mobilities are shown in Table I along with possible correlatives of the mobility. A temperature dependence of the relative mobility was observed and is shown in Fig. 2 for some of the ions. Measurements could not be made at temperatures significantly below 1.2 K because of the power dissipated in the discharge and filament, and above about 1.4 K it was difficult to keep the discharge stable—presumably because of the increased vapor pressure.

We can summarize our data as follows: (1) There appears to be no regular relationship between the mass of an ion and its mobility. (2) Ca, Sr, and Ba, which are in the second column of the periodic table, have mobilities higher than that of helium, while K, Rb, and Cs, which are

TABLE I. Experimental values of the impurity ion mobilities at 1.29 K, and several possible correlatives.

Ion	Mass (in units of M_{He})	Crystal ion radius[a] (Å)	First and second ionization potentials[a] (V)	Outer electron configuration of ion	$\frac{\mu^{-1}_{\mathrm{ion}}}{\mu^{-1}_{\mathrm{He}}}$
He	1	...	24.46, 54.14	$1S^1$	1.0
^{40}Ca	10.0	1.18	6.09, 11.82	$4S^1$	0.890 ± 0.001
^{48}Ca	12.0	1.18	6.09, 11.82	$4S^1$	0.899 ± 0.0015
Sr	21.9	...	5.67, 10.98	$4P^6 5S^1$	0.869 ± 0.003
Ba	34.4	1.53	5.19, 9.95	$5P^6 6S^1$	0.787 ± 0.001
K	9.8	1.33	4.32, 31.66	$3P^6$	1.039 ± 0.002
Rb	21.4	1.47	4.16, 27.36	$4P^6$	1.131 ± 0.002
Cs	33.2	1.67	3.87, 23.4	$5P^6$	1.125 ± 0.002

[a] Ref. 12.

in the first column of the periodic table, have mobilities lower than that of helium. (3) Within the group Ca, Sr, and Ba, the mobility increases with increasing atomic mass. (4) For the two isotopes of Ca, the mobility decreases with increasing mass, as one would expect from elementary considerations. (5) Within the group investigated, ions with relative mobilities larger than 1 have their relative mobilities decrease with increasing temperature, while those with relative mobilities smaller than 1 have their relative mobilities increase with increasing temperature. Mobilities seem to relax towards the helium mobility as the temperature is increased.

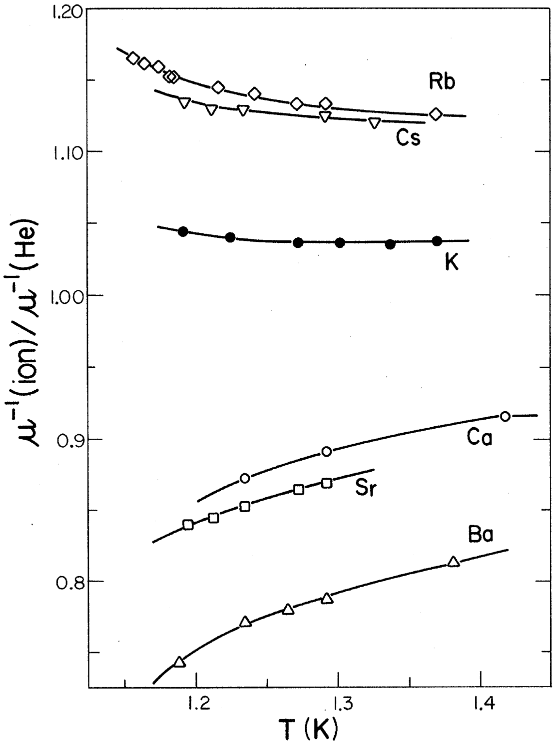

FIG. 2. Temperature dependence of the relative ion (inverse) mobility. The lines are aids to the eye.

In the positive-ion snowball model of Atkins, the snowball radius and the helium density in the vicinity of the ion are functions only of the charge of the ion, the polarizability of the helium, and the equation of state of helium. Aside from an effect associated with the mass of the ion, the ion mobility should be independent of the nature of the core ion. The most glaring inconsistency of our data with this last statement is the existence of heavy ions (Ca, Sr, Ba) with mobilities larger than that of helium. Elementary considerations suggest that for a given scattering cross section, the ion mobility should decrease with increasing mass. One might attempt to explain the Ca, Sr, and Ba data by suggesting that since these atoms are from the second column of the periodic table, they have particularly low double-ionization potentials, and what we ascribe to singly charged ions are in reality doubly charged ions. This explanation is felt to be inadequate for two reasons. First, if we see the doubly charged ion peak, we should certainly see the larger-amplitude singly charged ion peak, and we see no peaks that could be so ascribed. Second, the dependence of the mobility on atomic mass *within* the group Ca, Sr, and Ba is in the wrong direction.

In order to isolate the effect of mass on ion mobility from the effect of atomic number, two isotopes of calcium were investigated. Bowley[11] has calculated the effect of mass on ion mobility. Using his analysis, we find that the mass of the calcium ion needed to account for the observed mobility shifts due to a mass change of 8 amu is (65 ± 10)M_{He} or (85 ± 15)M_{He}, depending on the assumptions used in the calculation.[13] It is clear that the heavy ions are "dressed" with helium atoms in a manner similar to helium ions.

It is clear from our results that one cannot calculate an ion mobility by assuming a continuum snowball picture and simply putting in the appropriate core ion mass. We should like to suggest the following as a possible model for the ion. Since the "continuum" ion radius is about 6 Å, not too much larger than an interatomic distance at the surface of the ion, it is probably better to think of the ion in terms of discrete atomic shells. The average radius of the outermost shell depends on the radius of the innermost shell, which in turn depends on the details of the interaction between the core ion and that shell. The problem of calculating the ion radius then reduces to the very difficult molecular physics problem of calculating the radius of a macromolecular ion consisting of a core ion within a sheath of helium atoms. It is not unreasonable that an ion from the second column of the periodic table interacts particularly strongly with a surrounding helium shell since its outer electron is rather weakly bound compared to that of first-column ions. In this model, the ion radius would be an oscillating function of the inner-shell radius and one could conjecture that the helium ion radius is such that the outer shell can be pulled in significantly before another shell is formed. The opposite situation is also a possibility; a larger inner shell leading to a sloughing off of the outer shell and therefore a smaller cross section for the ion. In this latter situation, it is worth pointing out that the surface of the ion need not be perfectly spherical. Indeed the ion might be thought of as a tiny crystal. The outer shell might then be sloughed off in a quasicontinuous way as the inner shell increases in radius. A third, although less likely, possibility is that the radius of the inner shell affects the stability of the outer shell so that the effective boundary condition for roton scattering might vary from no slip to slip as the inner-shell radius varies. All of these effects will be somewhat masked, of course, by roton scattering from the excess density tail outside the liquid-solid interface. These suggestions are qualitative and rather speculative, but in any event it is clear that the electronic character of the core ion "penetrates" several atomic layers of helium atoms in affecting the ion-roton cross section.

We should like to thank Professor T. Tsuneto and Professor P. Leath for many useful discussions.

---

†Work supported in part by a grant from the National Science Foundation.

*Alfred P. Sloan Foundation Fellow.

[1] F. Reif and L. Meyer, Phys. Rev. 119, 1164 (1960).

[2] G. W. Rayfield and F. Reif, Phys. Rev. 136, A1194 (1964).

[3] W. I. Glaberson, J. Low Temp. Phys. 1, 289 (1969).

[4] W. T. Sommer, Phys. Rev. Lett. 12, 271 (1964).

[5] G. Baym, R. G. Barrera, and C. J. Pethick, Phys. Rev. Lett. 22, 20 (1969).

[6] C. G. Kuper, Phys. Rev. 122, 1007 (1961); for a more complete discussion, see R. J. Donnelly, W. I. Glaberson, and P. E. Parks, *Experimental Superfluidity* (Univ. of Chicago Press, Chicago, Ill., 1967).

[7] G. Ahlers and G. Gamota, Phys. Lett. 38A, 65 (1972); R. M. Ostermeier and K. W. Schwarz, to be published.

[8] A. J. Dahm and T. M. Sanders, Jr., Phys. Rev. Lett. 17, 126 (1966).

[9] K. R. Atkins, Phys. Rev. 116, 1339 (1959).

[10] G. G. Ihas and T. M. Sanders, Jr., Phys. Lett. 31A, 502 (1970).

[11] R. M. Bowley, J. Phys. C: Proc. Phys. Soc., London 4, 1645 (1971); we have recently become aware of a calculation by R. G. Barrera and G. Baym (to be published) which provides, in some limits, a mobility which increases with increasing mass. This result does not materially affect the conclusions of this paper.

[13] In terms of Bowley's calculations, the assumption of a constant cross section for scattering into different parts of the excitation spectrum leads to the first number while the assumption of a constant matrix element leads to the second.

[12] Values from *Handbook of Chemistry and Physics* (The Chemical Rubber Company, Cleveland, Ohio, 1966), 47th ed.; L. Pauling, *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, N. Y., 1960), 3rd ed., p. 514.