the role of screening in PSD.

In summary, we have presented PSD data for O^+ from Na_xWO_3 in the photon energy range 30 eV $< h\nu < 84$ eV and compared it with a CFS over a similar photon energy range. It was shown that the KF mechanism[1] applies to the system in the case of W core-level involvement. Further, lack of structures in the PSD spectrum at the Na $2p$ core threshold demonstrates for the first time bonding-site selectivity by the PSD technique. Finally, the correspondence of the PSD thresholds to the binding energies of the W core levels in *bulk* Na_xWO_3 indicates that the desorbing W sites have the same coordination as the bulk.

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Metastability and Nucleation of ^{3}He-^{4}He Mixtures near the Tricritical Point

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Homogeneous nucleation of phase separation has been investigated in liquid ^{3}He-^{4}He mixtures. Near the tricritical point the maximum supercooling marking the boundary of the metastable region is strongly enhanced compared to ordinary critical fluids. Beyond the metastability limit, the observed growth of the new phase is in good accord with a theory of Lifshitz and Slyozov.

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The condensed phases of helium have for a long time been playing a rather important role for the understanding of phase transitions. Equilibrium properties of pure liquid ^{4}He, but also of ^{3}He-^{4}He mixtures along the lambda line and near the tricritical point, have been widely studied, and the agreement between theory and experiment in general is excellent.[1,2] The same reasons which have favored liquid helium for these equilibrium investigations—like its extreme purity and the exceptionally simple constituents—ought to make it well suited also for studying states far from equilibrium. In particular, mixtures of ^{3}He-^{4}He because of their miscibility gap below the tricritical point offer the opportunity to investigate metastable states and nucleation in a phase-separating quantum system. Yet until recently experimental information about the behavior of helium mixtures in the miscibility gap was rather sparse. The only quantitative measurements in the vicinity of the tricritical point—an experiment by Brubaker and Moldover on the nucleation of phase separation in supercooled mixtures[3]—suggested a metastable region one order of magnitude smaller than anticipated on the basis of classical nucleation theory.[4] Considering such a discrepancy in an otherwise well-understood system we have begun to study metastability and the early stage of decomposition of ^{3}He-^{4}He quenched into the miscibility gap.

States inside the miscibility gap were prepared by the usual pressure quench technique,[5,6] starting from an equilibrium state on the coexistence curve at a pressure p_i and a temperature $T_i = T_t(p_i) - \Delta T$, where $T_t(p)$ is the (pressure-dependent) tricritical temperature. The beginning of phase separation, characterized by the appearance of rapidly growing concentration fluctuations, was detected by measuring the attenuation of a laser beam passing through the sample. Since the polarizability of helium and therefore the scattering from the fluctuations is relatively small, not only the onset of decomposition[7] as in previous experiments,[8-11] but also the subsequent droplet growth could be derived from the transmitted intensity. (In the systems studied previously multiple-scattering effects have prevented such a quantitative analysis.)

Figure 1 shows the transmitted intensity I_t and the effective quench depth $\delta T = T_t(p(t)) - T(t) - \Delta T$ as a function of time. The time dependence of δT is determined by the pressure relaxation through the sample chamber capillary. Several stages can be distinguished: Initially $I_t(t)$ agrees with I_0, the transmitted intensity before the start of the quench, within the accuracy of our measurement; then, at some supercooling δT_m a sharp decrease in I_t is observed, followed by a slower variation and, at much later times, a further accelerated decrease in transmissivity.

When in the course of the pressure release the quench depth reaches the value δT_m the nucleation rate apparently increases rapidly so that the time for nucleation embryos[10] to develop becomes very small on the time scale given by the speed of our quench. We therefore identify δT_m with the cloud point known from other systems,[8-11] which implies that in the temperature interval $\delta T < \delta T_m$ the mixture is in a metastable state. Indeed, states prepared with a quench depth $\delta T < \delta T_m$ did *not* decay during the sampling interval of several seconds. The normalized maximum supercooling $\delta T_m/\Delta T$ where the experimental limit of metastability is reached depends on the reduced temperature as plotted in Fig. 2. According to the classical nucleation theory by Becker and Döring[4] the maximum supercooling in the metastable state is $\delta T_m/\Delta T \sim 0.13$. Our measurements show that for $\epsilon = (T_t - T)/T_t > 0.03$ the metastable regime determined here is actually in very good agreement with this prediction, both for the superfluid and

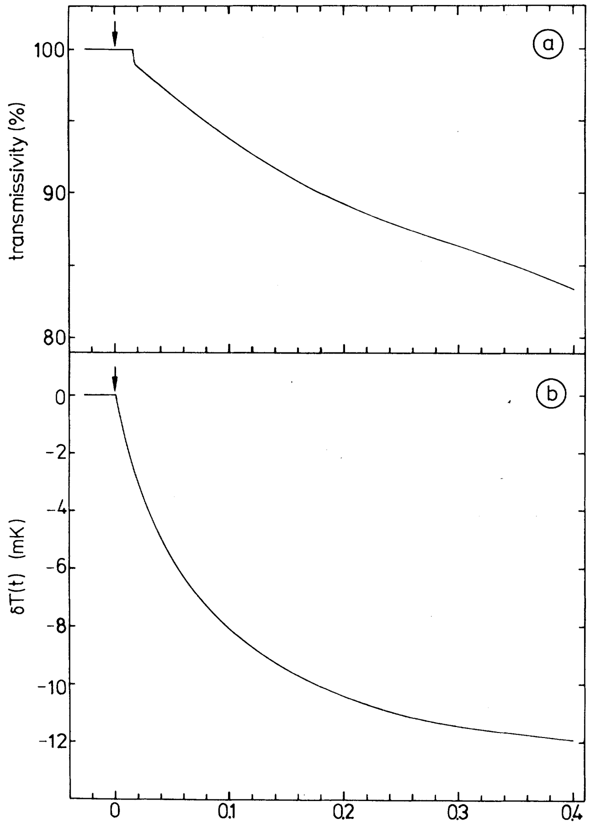

FIG. 1. (a) Transmissivity I_t and (b) effective quench depth δT of a ^{3}He-^{4}He mixture during a pressure quench into the miscibility gap. The quench started from the superfluid branch of the coexistence curve at $\Delta T = 14$ mK. The pressure was released here from $p_i = 0.7$ bar to p_f = saturated vapor pressure ~ 0 bar. The arrows mark the beginning of the quench.

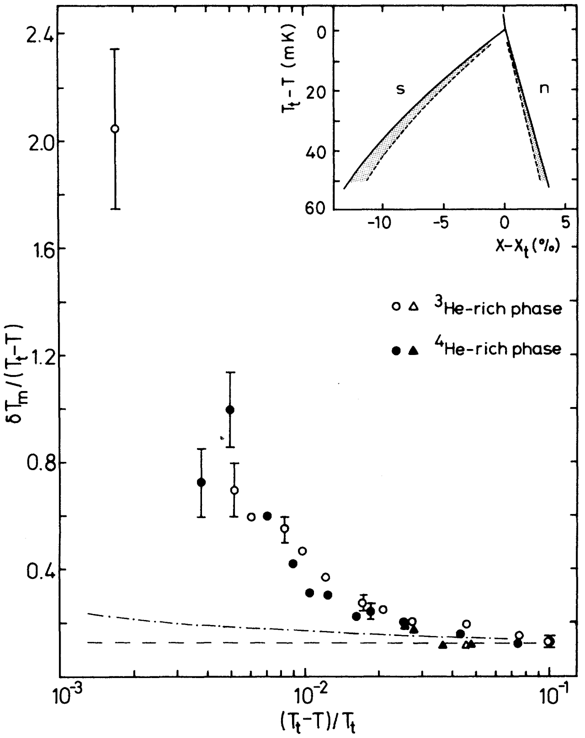

FIG. 2. Relative maximum supercooling $\delta T_m/\Delta T$ vs reduced temperature for both branches of the coexistence curve. The speed of the quench at the onset of nucleation was between 150 and 200 mK/s for the circles and one order of magnitude smaller for the triangles. The dashed line corresponds to the classical nucleation theory (Ref. 4), whereas the dash-dotted line respresents the supercooling in four other systems as shown in Fig. 2 of Ref. 10. In the phase diagram (inset) the metastable regimes adjacent to the superfluid (s) and the normal (n) phase are indicated by the shaded areas.

the normal branches of the coexistence curve. Since here in contrast to the experiment of Brubaker and Moldover[3] the influence of walls is mostly eliminated, because only a small volume near the center of the sample cell is probed by the laser beam (diameter 0.2 mm), the distinctly smaller metastable regime found earlier might be attributable to heterogenous nucleation.

The striking feature in Fig. 2 is that close to the tricritical point the metastable region is considerably *larger* than predicted by the classical nucleation theory. An apparent increase of stability has been noticed already in earlier experiments for ordinary fluids,[8-11] where this phenomenon has been ascribed to critical slowing down by Binder and Stauffer[12] and, in more detail, by Langer and Schwartz.[13,14] In ^{3}He-^{4}He, though, for $\epsilon \to 0$ the apparent metastability increases much more rapidly than for the ordinary fluids, as shown by the comparison in Fig. 2. This feature could be a peculiarity of tricritical systems: There critical slowing down, reflected in the width Γ of the Rayleigh line, is very pronounced with $\Gamma \propto \epsilon^{0.95\pm0.07}$ as compared to the usual behavior $\Gamma \propto \epsilon^{0.67}$.[2]

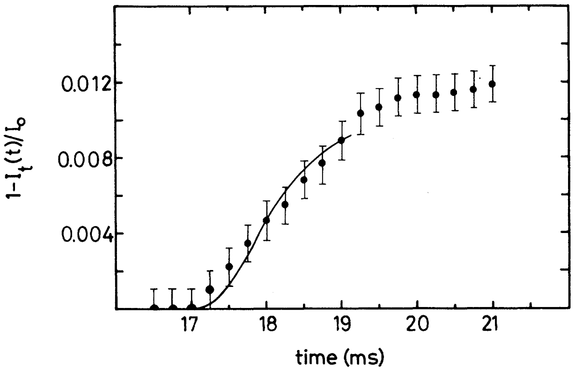

FIG. 3. Normalized total scattered intensity $I_s/I_0 = 1 - I_t/I_0$ during the early stage of decomposition of the same quench as in Fig. 1. The solid line was calculated with Eq. (1) and a Mie-scattering formula from Ref. 17. Since I_s/I_0 is only of the order of 10^{-2}, multiple scattering is negligible here.

As already noted, an analysis of the transmitted intensity $I_t(t)$ also yields information about the droplet growth of the new phase after the initial stage of nucleation. As an example we have plotted in Fig. 3 data from Fig. 1 on an expanded scale. The quantity $1 - I_t(t)/I_0$ is equal to the normalized total scattered intensity $I_s(t)/I_0$, since multiple scattering is negligible here. The increase in scattered intensity, which is due to the growth of the droplets, levels off at about 2.5 msec after the onset of nucleation. We interpret this behavior as the completion of phase separation on a microscopic scale, where, apart from the interfaces between the droplets and the background phase, the mixture locally has nearly reached the equilibrium states on the coexistence curves.

The subsequent relatively slow decrease of the transmitted intensity [see Fig. 1(a)] results from the growth of the volume fraction of the minority phase, i.e., the droplets. Finally, the crossover to an again accelerated decrease marks the regime of coalescence which has been investigated earlier.[5,6] At this stage a contracting halo in the scattered intensity is observed, which signifies that the clusters formed by the new equilibrium phase become spatially correlated due to the coalescence mechanism.

We have compared our data with a theory of Lifshitz and Slyozov for the growth of droplets in a supersaturated mixture.[15] According to these authors the variation of the radius R of a droplet is implicitly given by

$$\frac{dR}{dt}=\frac{D}{R}\left(\frac{\delta x}{\Delta x}-\frac{2d_0}{R}\right). \qquad (1)$$

Here D is the diffusion coefficient, $\delta x(t)$ is the instantaneous supersaturation, Δx is the concentration difference of the two coexisting phases in equilibrium, and $d_0=\frac{1}{6}\xi$,[13] where ξ is the correlation length. From Eq. (1) we have calculated an average droplet radius $\overline{R}(t)$, assuming that in the range considered here the droplet distribution is sharply peaked at $\overline{R}$, and that the number density of the droplets has a constant value n_d, i.e., that nucleation occurs essentially in a very short time interval ($\Delta t \ll 2.5$ msec) at the beginning of the decomposition process. Both assumptions appear to be well fulfilled for other systems[13, 16] in the regime where the speed of the decomposition reaction, given by the change in supersaturation $d(\delta x)/dt$, is near its maximum value. The density n_d which enters the calculation was determined from the nearly constant light-scattering signal after the reaction has gone close to completion (see Fig. 3, $t \gtrsim 20$ msec). The resulting normalized scattered intensity $I_{\text{theor}}(t)$ is given by the solid line in Fig. 3. For the material parameters we have taken the values measured on the coexistence curve.[1,2] The agreement with the data is quite remarkable, which suggests that in the metastable regime quantities like the diffusion coefficient have values comparable to those on the phase separation lines. Similar conformity has been found also for other quenches in the range $0.013 \leqslant \epsilon \leqslant 0.07$.

In summary, our measurements have established a metastable region in the phase diagram of ^{3}He-^{4}He mixtures near the tricritical point, which expressed in $\delta T_m/\Delta T$ is symmetric for the superfluid and the normal phase. For quenches beyond the metastability limit droplets appear whose growth up to the microscopic completion of phase separation closely follows a Lifshitz-Slyozov behavior. We conclude that in the temperature interval investigated here the onset of phase separation occurs via a fast nucleation process; the competing mechanism for phase separation, spinodal decomposition as considered by Hohenberg and Nelson,[18] thus appears to become relevant in ^{3}He-^{4}He only for temperatures extremely close to T_t.

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