Phase diagram of the itinerant helimagnet MnSi from high-pressure resistivity measurements and the quantum criticality problem

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We performed a series of resistivity measurements on a MnSi single crystal at high pressures, created by a piston-cylinder device with a liquid pressure medium. The form of the resistivity curve at ambient pressure clearly indicates a first-order nature of the magnetic phase transition in MnSi. Application of high pressure rapidly degrades the first-order features of the phase transition. The temperature derivative of resistivity demonstrates two notable features of the phase transition that disappear on increasing pressure: a sharp peak marking the first-order phase transition and a shallow maximum situated slightly above the critical temperature and pointing to prominent helical fluctuations. The current experimental data rule out any strong first-order phase transition in MnSi at high pressures and low temperatures, which would prevent development of a quantum critical region. On the contrary, there should exist true quantum critical phenomena in MnSi at high pressures because a weak first-order transition, if it survives at high pressures to the lowest temperatures, should not suppress the entire quantum critical region.

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I. INTRODUCTION

Manganese silicide MnSi a remarkable example of a helical magnet with the Dzyaloshinski-Moria interaction has attracted much experimental and theoretical interest. Despite extensive efforts, many important features of the temperature-pressure (T-P) phase diagram of MnSi are not well understood. Nevertheless, there is a general belief that a ferromagnetic phase transition inevitably becomes first order as it is tuned toward zero temperatures, therefore avoiding development of quantum criticality. Still, it is not clear how the magnetic phase transition in MnSi evolves along the transition line and what are properties of the phase transition in the high-pressure low-temperature limit. This ambiguity is reflected in the evolution of points of view that is summarized briefly below and reviewed in more detail in Ref. 1.

A magnetic phase transition of unidentified nature in MnSi at about 30 K was reported initially in Ref. 2 and subsequently was identified as a phase with a helical spin order.[3] Studies of the heat capacity and thermal expansion of polycrystalline and single-crystal samples of MnSi seemingly demonstrated a continuous (second-order) phase transition,[4] a view adopted for several years even though some evidence suggested[5] that the phase transition might be first order. Early high-pressure experiments showed that the phase transition temperature could be tuned toward zero at pressures of about 1.4 GPa.[6] Later studies at high pressures, however, found a dramatic change in behavior of the ac magnetic susceptibility along the phase transition line. A peak in the magnetic susceptibility of MnSi at the phase transition evolved into a simple step at $\sim$1.2 GPa and $\sim$12 K, which was interpreted as an indication of a tricritical point where a second-order phase transition became first order.[7,8] The tricritical idea found theoretical support[9] in an argument that generically favored a first-order phase transition in itinerant ferromagnets at low temperatures, which would preclude quantum critical phenomena. Application of this idea to MnSi led to the concept of a new quantum state of matter (non-Fermi liquid metal without quantum criticality[10]). Later it was shown, however, that the disappearance of the peak in magnetic susceptibility at the phase transition was most probably caused by nonhydrostatic pressure conditions.[11]

A careful study of a good quality single crystal of MnSi[12,13] revealed sharp peaks (dips) in the temperature derivative of resistivity, the heat capacity, and thermal expansion coefficient that led to the conclusion of a weak first-order character of the phase transition at ambient pressure. Ultrasound measurements, performed by the same group, confirmed this conclusion;[14] whereas, small angle neutron scattering experiments provided independent proof for a first-order phase transition in MnSi.[15] The experiments[12–14] also solidly confirmed features (a sharp peak and a shoulder) in the thermal expansion coefficient and sound absorption reported earlier.[16,17] Some even earlier heat capacity measurements[18] also revealed a shoulder on the high-temperature side of the peak, which became less prominent with increasing residual resistivity ratio (RRR). As a result, the existence of the shoulder was ascribed to sample imperfection,[18] but we note that lengthy annealing of MnSi, while improving the RRR, also leads to degradation of the phase transition. Though mounting evidence[12–14] proving that the transition was first order at ambient pressure initially was ignored in favor of a tricritical scenario, the first-order character of the phase transition in MnSi at ambient pressure has become recognized widely.[15,19–21] The current view of MnSi at ambient pressure is that it undergoes a first-order magnetic transition near 29 K with a tiny volume discontinuity $-\Delta V/V \approx 3 \times 10^{-6}$ Ref. 12. At $T = 2$–5 K and $P = 1.5$ GPa, a volume change at the phase transition reaches a value almost two orders of magnitude higher $-\Delta V/V \approx 2 \times 10^{-4}$ Refs. 10 and 22. The questions raised by these results are what is the connection between these two values of volume change and how can this increase of the volume discontinuity at elevated pressures be related to the evolution of the phase transition in MnSi?

Let us consider two possible scenarios for the evolution of the first-order transition in MnSi along the phase transition line. (1) The first-order phase transition continues with applied pressure down to the lowest temperature, and a polycritical point does not exist along the phase boundary. This scenario seems hard to reconcile with the above-mentioned values of the volume discontinuities. (2) The first-order phase transition, which is driven in the current case to be first

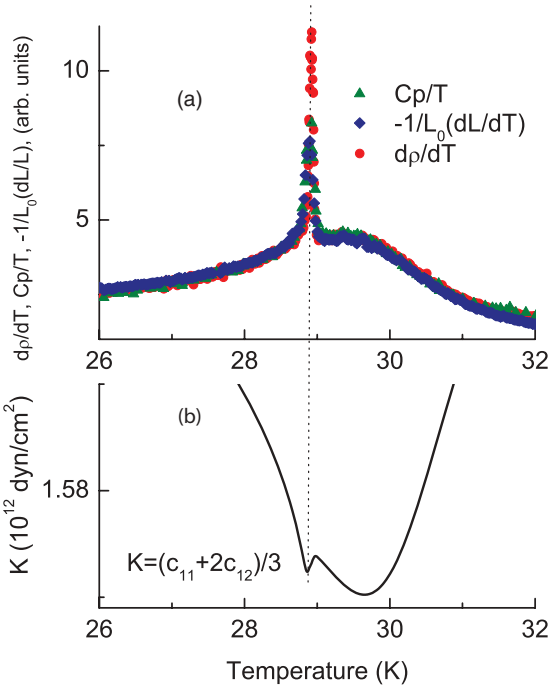

FIG. 1. (Color online) (a) Reduced heat capacity divided by temperature C_p/T, linear coefficient of thermal expansion $1/L_o(dL/dT)$, temperature derivative of resistivity $d\rho/dT$, and (b) bulk modulus K of MnSi as functions of temperature in the vicinity of the phase transition at ambient pressure.

order by fluctuations,[5] evolves into a second-order one as thermal fluctuations are suppressed at elevated pressures and lower temperatures. In this case, there would be a tricritical point on the phase transition line that excludes any steplike volume discontinuity in the low-temperature limit. Quantum fluctuations should be suppressed as well due to an increased effective dimensionality of the quantum system, but this may not be true in the special case of MnSi.[23]

II. EXPERIMENTAL

In an attempt to resolve the issue of the evolution of the phase transition in MnSi, we performed a series of resistivity measurements on a MnSi single crystal at high pressures. The reason for this choice lies in the observation of almost perfect scaling between the temperature derivative of resistivity, thermal expansion coefficient and heat capacity[13] [see Fig. 1(a)]. Consequently, the resistivity also reflects thermodynamic properties of the phase transition, but one should keep in mind that the first-order transition in MnSi is just a minor feature on the extended thermodynamic anomaly. Figure 1(b), displaying the bulk modulus of MnSi as a function of temperature, just emphasizes this fact. In the present study, we intentionally employed a classical high-pressure piston cylinder technique, analogous to that used in Refs. 10 and 22, with silicon liquid as a pressure medium. The single-crystal sample was cut from the same batch used in previous experiments.[11–13] The resistivity was measured by a standard four-terminal dc technique. Temperature was registered with a Cernox sensor, and pressures were calculated from known coordinates of the T-P phase transition line of MnSi.

We do not show a complete set of resistivity curves obtained in the current experiment. Instead, Fig. 2 displays only limited parts of the resistivity curves in the vicinity of the phase transition. The temperature dependence of the resistivity at ambient pressure clearly shows the first-order nature of the magnetic transition in MnSi [see Fig. 2(a)]. We emphasize the narrow temperature interval of the phase transition [$\sim$0.04 K Fig. 2(a)]. Figures 2(b)–2(e) show the fast degradation of the first-order signature of the phase transition with pressure. Finally, at a pressure of about 1 GPa, there no longer is a trace of the first-order transition. We will discuss this issue later.

Figure 3(a) illustrates the evolution of the temperature derivative of resistivity $d\rho/dT$ of MnSi along quasi isobars, where the data span the phase transition boundary. The data, obtained with helium as a pressure medium,[11] are reproduced in Fig. 3(b) for comparison. As is seen in Fig. 3(a) at low pressure, $d\rho/dT$ has a now well-known form with a sharp peak followed by a shallow shoulder on the high-temperature side of the peak. This sharp peak in $d\rho/dT$ identifies a first-order phase transition [see Fig. 2(a) for confirmation]. On application of pressure, the sharp peak starts to smear and completely disappears between 0.8 and 1.0 GPa in correspondence with Fig. 2. At first sight, it might suggest a change of order of the phase transition; however, there are clear indications of the disruptive influence of nonhydrostatic stresses on the phase transition. Indeed, the return run at a pressure 0.6 GPa shows an essential deformation in the shape of $d\rho/dT$ after loading the sample to $\sim$1 GPa. Unfortunately, the experiments with helium were not extended to higher pressures due to technical problems [see Fig. 3(b)].

From a comparison of Figs. 3(a) and 3(b), it is hard to make a definitive conclusion on whether the frozen silicon liquid is inferior to solid helium as a pressure medium. This is

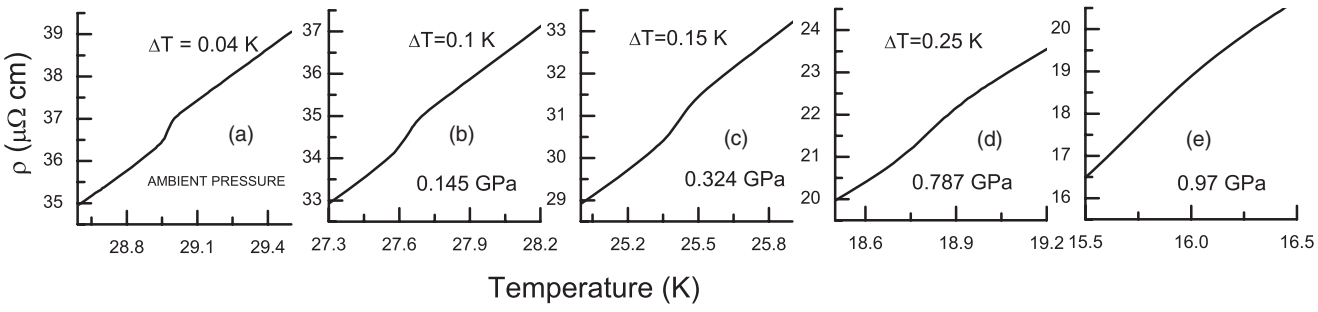

FIG. 2. Resistivity change at the phase transition in MnSi. ΔT is the temperature width of the phase transition.

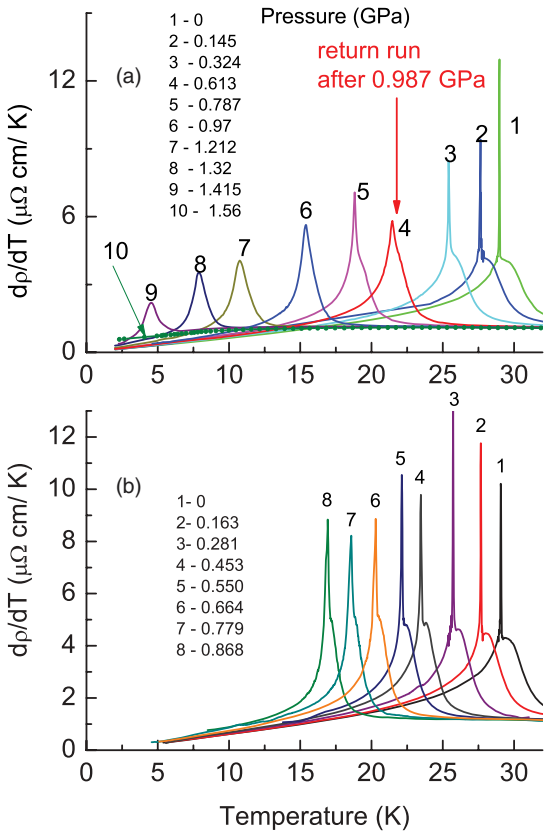

FIG. 3. (Color online) Temperature derivatives of resistivity $d\rho/dT$ at the phase transition in MnSi at different pressures. (a) Current data, obtained with a liquid pressure medium, and (b) data obtained with helium as a pressure medium.[11]

emphasized in Fig. 4 where two curves of $d\rho/dT$ are plotted from silicon and helium experiments at the same pressure. Surprisingly, these two curves differ very little. Thus we are unable to state whether the sharp peaks in $d\rho/dT$ disappear because of nonhydrostatic stresses and/or some fundamental physics also is involved. We may conclude, however, that a sharp first-order transition in MnSi is not seen and probably cannot be seen in experiments at pressures higher than 0.8–1.0 GPa with frozen liquids as a pressure medium (see Fig. 2). We also note that a sharp peak in the thermal expansion coefficient of MnSi was not seen[10,22] even at ambient and low pressures due to insufficient resolution.

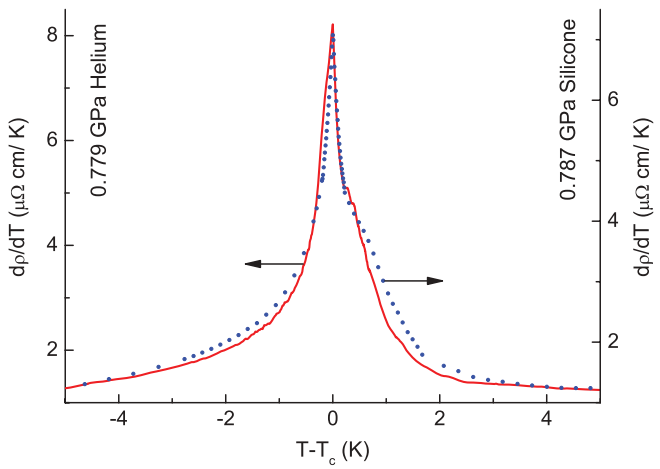

FIG. 4. (Color online) Comparison of temperature derivatives of resistivity $d\rho/dT$ of MnSi, obtained in two different pressure media (helium and silicone liquid).

III. DISCUSSION

So what is a nature of the low-temperature volume anomaly?[10,22] First, we point out that the magnetic transition in MnSi is accompanied by continuous anomalies in thermodynamic and transport properties induced by spin fluctuations,[24] see Fig. 1. At high pressures and lower temperatures, these anomalies should become progressively less extended as the fluctuations become frozen out. Finally, at these pressures and temperatures, thermodynamic and transport anomalies may be well defined and look like smeared discontinuities, therefore imitating a first-order phase transition. These conclusions are well illustrated by Fig. 5 that displays resistivity isotherms crossing the phase transition, constructed from the quasi-isobaric temperature-dependent resistivity measurements. As seen in Fig. 5, the resistivity anomaly at the phase transition at low temperature is within ~0.1 GPa of the phase transition, in agreement with results of Refs. 10 and 22. Though one should be cautious trying to draw an exact relation between volume and resistivity in the quantum regime, a volume anomaly by definition is accompanied by a resistivity feature at temperatures above zero. Thus claims of experimental observations of a first-order phase transition in MnSi at low temperatures and high pressures are certainly not valid. Instead, the volume anomaly reported earlier[10,22] likely is caused by the spin fluctuations which cannot be classified as a phase transition. This statement is illustrated in Fig. 6, demonstrating a relationship between the volume anomaly and the phase transition in MnSi at ambient pressure. As seen in this figure, the huge volume anomaly, spreading from almost zero to ~35 K, practically conceals the tiny first-order phase transition (see Fig. 6 and the insert). This transition becomes

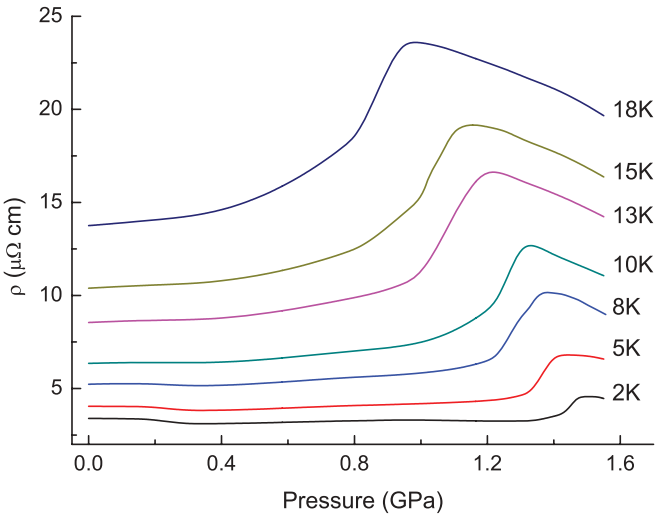

FIG. 5. (Color online) Resistivity isotherms of MnSi showing an evolution of the fluctuation region in the vicinity of the phase transition.

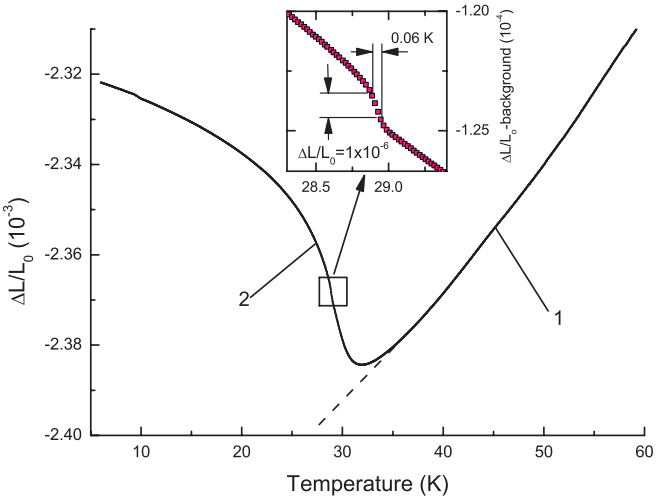

FIG. 6. (Color online) Linear thermal expansion of MnSi illustrating a relationship between the volume anomaly and the first-order phase transition. Curve 1 is the "normal" branch with positive thermal expansion, curve 2 is the fluctuation branch with negative expansion, and L_o is the room temperature value. Modified from Ref. 12.

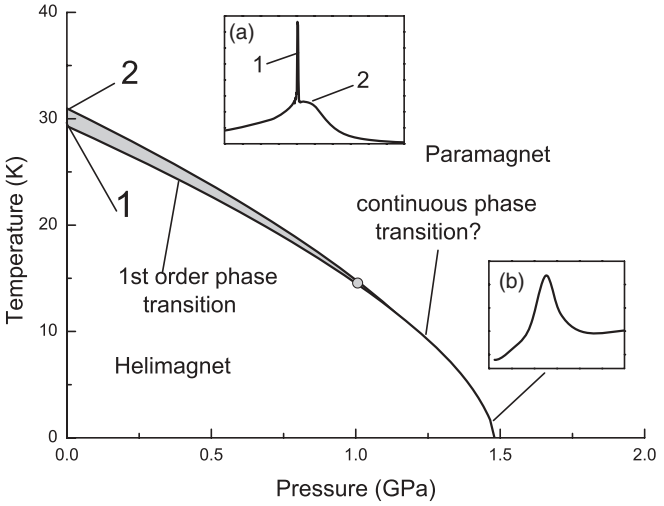

FIG. 7. Tentative phase diagram of MnSi at high pressure. The grey region shows the helical fluctuation domain, disappearing at a pressure of ∼1 GPa. The grey circle could be a tricritical point, if the phase transition at pressures >1 GPa is truly continuous. (a) and (b) illustrate variations of the form $d\rho/dT$ with pressure.

unobservable at pressures greater than 1 GPa, and only the squeezed volume anomaly can be seen at higher pressures, as reflected in the resistivity behavior (see Fig. 5.)

Returning to the phase transition evolution one should be aware of two notable features that disappear with decreasing temperature. They are the sharp peak marking the first-order phase transition and the shallow maximum, situated slightly above the critical temperature and pointing to a prominent role of helical fluctuations[15,25,26] (see Fig. 1). As a result, at low temperature, the phase transition in MnSi is manifested by almost symmetric and rather steep maxima in the temperature derivatives of resistivity. The current experimental data obviously rule out any strongly first-order phase transition at $T \rightarrow 0$ in MnSi, though a weak, smeared first-order phase transition may be hidden at the slopes of the maxima. The tentative phase diagram of MnSi is displayed in Fig. 7.

It is tempting to connect the features of the suggested phase diagram with experimental and theoretical data, describing the spin structure of MnSi in different P-T conditions. Unfortunately, despite numerous neutron scattering investigations there is no a general consensus on a spin structure of the magnetically disordered phase of MnSi. About the same small angle neutron scattering data are interpreted in somewhat different ways. Grigoriev *et al.* interpret the domain situated just above the Curie point in MnSi at ambient pressure simply as a spin system with strong chiral fluctuations.[25,28] At the same time Pappas *et al.* believe in a skyrmion like spin structure of the domain,[15,26] whereas Hamann *et al.* claim a magnetic blue phase structure in MnSi above the Curie point at ambient pressure.[20] Hamann *et al.* also state that a diffraction pattern of MnSi at high pressures and low temperatures with so called partial order, observed in Ref. 29, is similar to that of the magnetic blue phase structure. Though the anisotropic distribution of scattering intensity in MnSi at high pressure raises some questions. Some blue phase features were declared for the partial-order phase MnSi in theoretical papers.[30,31] A skyrmion columnar texture is suggested for the non-Fermi liquid domain in Ref. 32. A fresh view of the nature of the partial-order phase of MnSi is proposed in the paper,[33] where specifics of the partial order are associated with quantum fluctuations.

The general impression is that on the phase transition at ambient pressure MnSi transforms to the matter with strong helical fluctuations, probably not having a certain static spin structure (the gray region in Fig. 7). These fluctuations may trigger the first-order phase transition, observed at low pressures. At high pressure and low temperature, the thermal fluctuations are frozen out (the grey region ceases to exist at pressures higher ∼1 GPa in Fig. 7) and a quasistatic spin structure emerges in the non magnetic phase of MnSi resembled a nematic liquid crystal.[29]

As emphasized, we are unable to distinguish between a first-order phase transition smeared by nonhydrostatic stress and a second-order phase transition. An evolution of the first-order phase transition in MnSi along the phase boundary is illustrated in Fig. 2. In the case of a true second-order transition at high pressures, we should have a tricritical point corresponding to the evolution from a weakly first-order transition at high temperatures to a second order one at low temperatures. This is quite opposite to former suggestions.[7–9] We place a provisional tricritical point at 16 K and 1 GPa (see Fig. 7), where the helical fluctuation domain disappears. We reiterate that the helical fluctuation domain is situated in a narrow temperature interval between the helically ordered phase and the paramagnetic phase. The simultaneous disappearance of this strongly fluctuating domain and first-order features in the phase transition emphasizes a connection between fluctuations and the first-order nature of the phase transition at ambient pressure. At the same time, this may prove the inability of quantum fluctuations to influence the order of the phase transition. We conclude then that there should exist true quantum

critical phenomena in MnSi at $T \to 0$ because the very weak first-order transition, if it survives to the lowest temperatures, cannot suppress the entire quantum critical region.

IV. CONCLUSION

In summary, the sharp peaks and shallow shoulders in the temperature derivatives of resistivity of MnSi, which indicate a first-order phase transition and a helical fluctuation domain, respectively, disappear simultaneously at 16 K and 1 GPa. This may imply the existence of a tricritical point on the phase transition line. On the other hand, it may mean that the first-order phase transition, being smeared by nonhydrostatic stresses in a frozen liquid, continues to the lowest temperatures. Note that in fact the imaginable conflict expected earlier between the volume discontinuity at ambient pressure and the high-pressure low-temperature volume anomaly does not exist at all because these discontinuities are related to different physical phenomena. In either case, the present experimental data do not support the idea of a strong first-order transition in MnSi at $T \to 0$, which would prevent development of the quantum critical region. In contrast, there is evidence for quantum criticality in MnSi in the form of a non-Fermi liquid resistivity at high pressures,[27] but more experimental work is needed to justify this conclusion. In particular, careful heat capacity and compressibility (sound velocity) measurements seem to be most relevant for resolving this issue, though those measurements at high pressures and low temperatures present a real challenge to experimentalists.

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