Comments

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Comment on the enhanced magnetic susceptibility of expanded liquid cesium

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A maximum in the enhanced magnetic susceptibility of liquid cesium at low densities is shown to be related to a Curie-law limitation of the susceptibility at the high experimental temperatures. Implications for the nature of the enhancement are discussed and it is shown that the available experimental results support a description of low-density cesium as a highly correlated, nearly antiferromagnetic metal.

Considerable interest has developed in the electrical and magnetic properties of liquid alkali metals expanded by heating toward the liquid-gas critical point. Because the critical densities are about 20% of the normal liquid or solid densities, large density variations can be achieved experimentally before the metallic properties give way to a metal-nonmetal transition close to the critical point.[1,2] As elemental monovalent metals, expanded alkali metals approximate the expanded alkali crystals considered by Mott[3] in his original discussion of the metal-nonmetal transition, and they are well suited for investigating electron correlation effects in low-density metals.[4]

Much of the recent activity was motivated by the remarkable results of Freyland[5] who measured the magnetic susceptibility of expanded cesium along the liquid-gas coexistence curve over a density range of roughly $0.6 < \rho < 1.8$ $g\,cm^{-3}$. With decreasing density, there develops a growing enhancement of the susceptibility which reaches a maximum at about 0.8 $g\,cm^{-3}$. This density is roughly twice the critical density ρ_c. Similar enhancements have subsequently been observed over more limited density ranges for rubidium[6] and sodium[7] although for these metals no peak in the susceptibility was found.

Enhanced susceptabilities at low density are in general accord with theoretical expectations for increased effects due to electron-electron interactions. According to the Stoner model of exchange enhancement, widely accepted for descriptions of the susceptibility at normal densities,[8] the enhancement of χ relative to the susceptibility χ_0 for noninteracting electrons is

$$\chi/\chi_0 = [1 - JN_a(E_F)]^{-1} \ , \tag{1}$$

where J is the exchange-correlation integral and $N_a(E_F)$ is the density of states per atom at the Fermi energy. For normal cesium, $\chi/\chi_0 \simeq 1.8$.[9] Since $N_a(E_F)$ should increase due to band narrowing, Eq. (1) predicts increased enhancement at low density. A divergence in χ when the bracketed expression of Eq. (1) vanishes might, at high temperature, take the form of a peak such as that observed for cesium. However, calculations by Rose[10] predict that the maximum enhancement should occur at the metal-nonmetal transition, i.e., at a density roughly half that of the observed peak. Rose suggested that increasing structural disorder in the expanded liquid might reduce the susceptibility at the lowest densities and produce a peak before the metal-nonmetal transition is reached.

Alternatively, Freyland[5] suggested that electron correlation effects enhance the susceptibility in the manner predicted by Brinkman and Rice.[4] The susceptibility enhancement in a highly correlated metal takes a form different from Eq. (1) and is described in terms of an enhancement of the density of states or effective mass[4]

$$\chi/\chi_0 = N(E_F)/N_0(E_F) = m^* \ . \tag{2}$$

In contrast with the Stoner picture, an enhanced specific heat is predicted to accompany the susceptibility enhancement for a highly correlated metal. Freyland[5] suggested that the susceptibility peak in cesium might be due to the competing effects of increased correlation enhancement and development of a Hubbard pseudogap[11] which lowers $N(E_F)$ as the metal-nonmetal transition is approached.

It is the purpose of this Comment to point out that the peak in the susceptiblity has a simple explanation which has apparently been overlooked. The experimental susceptibility, converted to volume susceptibility units and corrected for diamagnetism,[12] is shown in Fig. 1. Also shown is the free-spin Curie susceptibility χ_{Curie} calculated for the appropriate densities and temperatures along the coexistence curve. It is clear that the observed susceptibility is limited by the Curie value and follows the Curie law within about 15% on the low-density side of the peak. The small apparent discrepancy in magnitude is consistent with inherent errors in the measured susceptibility, temperature, and density, and the estimated diamagnetic correction. The absence of similar peaks in the observed susceptibilities of sodium and rubidium[6,7] is readily understood since the susceptibilities are still well below the Curie limit at the minimum densitites reached for those metals. Interestingly, extrapolation of the rubidium data[6] indicates that the Curie limit would be reached at roughly the same reduced density $\rho/\rho_c \simeq 2$ as for cesium.[13] It is clear, however, that the susceptibility peak is essentially a consequence of the high temperature at which the experiments must be conducted. The density value at the peak therefore has no special significance in the context

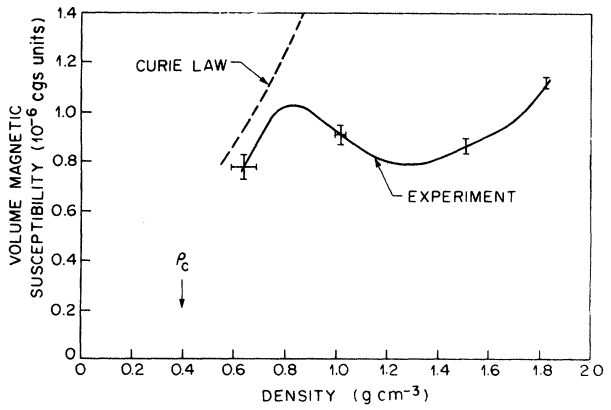

FIG. 1. Volume paramagnetic spin susceptibility vs density for liquid cesium along the liquid-gas coexistence curve. Solid line: experimental results of Freyland (Ref. 5) corrected for ion core and conduction-electron diamagnetism. Typical experimental uncertainties in susceptibility and density are indicated. Broken line: free-spin Curie susceptibility calculated for densities and temperatures along the coexistence curve.

of theories in which it is assumed that the temperature is 0 K.

The simple explanation that the low-density susceptibility of cesium is limited by the Curie law has nontrivial implications for interpretation of the enhancement. The exchange-enhanced susceptibility represented by Eq. (1) is not restricted to $\chi < \chi_{\text{Curie}}$ and, in fact, can increase without limit on approaching a transition to ferromagnetism. On the other hand, an enhanced density of states as in Eq. (2) leads to a reduced degeneracy temperature, and χ cannot exceed χ_{Curie} even in the strongly enhanced limit. This behavior is described by integrals over the Fermi function $f(E)$

$$\frac{\chi}{\chi_{\text{Curie}}} = \frac{-kT\int_0^\infty dE\,(df/dE)N(E)}{\int_0^\infty dE\,f(E)N(E)}\,, \tag{3}$$

and, for a free-electron-like band $N(E)\alpha m^{*3/2}E^{1/2}$, it is easily shown that $\chi/\chi_{\text{Curie}} \to 1$ for sufficiently large m^*. Evaluation of Eq. (3) under the conditions of the expanded cesium experiments indicates that $m^* \simeq 6.5$ at $\rho = 0.8$ g cm^{-3}. According to the Brinkman-Rice theory, this value of the mass implies a value $\xi \simeq 0.08$ for the fraction of doubly occupied sites.[4]

The low-temperature magnetic state of a highly correlated metal is predicted to be antiferromagnetic.[4,11] Spin-density functional calculations of the ground-state energy of expanded hydrogen and alkali-metal crystals also yield an antiferromagnetic state.[10,14,15] The observed magnetic properties of expanded liquid cesium support these predictions. Analysis of the ^{133}Cs nuclear-spin-relaxation rates and Knight shifts revealed a change in the wave-vector (q) dependence of the susceptibility enhancement leading toward increased enhancement at high q relative to $q = 0$.[9] The same effect has been reported recently for expanded liquid sodium.[7] Such an increase in high-q enhancement corresponds to a trend from Stoner-type (ferromagnetic) enhancement to antiferromagnetic enhancement. Thus the inferred density dependence of the q-dependent susceptibility is completely consistent with the Curie-law behavior of the uniform ($q = 0$) susceptibility at low density. The magnetic properties of the expanded alkali metals are essentially those of a highly correlated, nearly antiferromagnetic metal or an antiferromagnet well above its ordering temperature.

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