Magnetic susceptibility of expanded fluid alkali metals

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From a phenomenological treatment of a correlation-induced metal-insulator transition at elevated temperatures, an interpretation of the behavior of the magnetic susceptibility of expanded fluid alkali metals is proposed. Renormalization of the Fermi temperature due to correlation is shown to play an essential role. An important conclusion is that the momentum distribution at the Fermi surface is quantitatively very different from that in jellium at the same density.

There has been much interest, both theoretical and experimental, in the magnetic properties of highly correlated systems. In particular, expanded alkali metals provide excellent subjects for the investigation of the influence of electron correlation on electrical and magnetic properties, and its role in the metal-insulator transition, which, for these materials, is believed to occur near to the liquid-vapor critical region.[1] The experiments of Freyland and co-workers[2-4] on the magnetic susceptibilities of alkali metals along the liquid-vapor coexistence curve have stimulated much interest, and it is on these that this note is focused. Warren[5,6] extracted the paramagnetic contribution to the total susceptibility due to the conduction electrons, and pointed out that the behavior in the low-density liquid region is consistent with a correlation-enhanced Pauli paramagnetism, limited by the free-spin Curie value. This is illustrated in Fig. 1, which incorporates the recent determination of the liquid-vapor coexistence curve for cesium by Jüngst, Knuth, and Hensel.[7] In what follows, we consider the behavior of the magnetic susceptibility in the vicinity of the metal-insulator transition, initially by means of a phenomenological description, and then by utilizing a microscopic theory developed for heavy-electron systems.

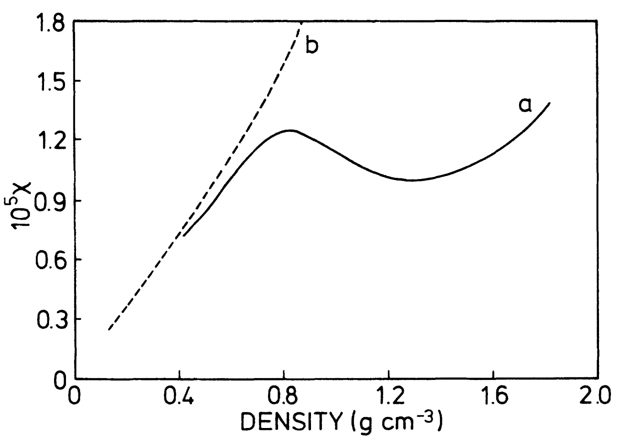

FIG. 1. Volume magnetic susceptibility (SI units) of expanded liquid cesium along the liquid-vapor coexistence curve (Ref. 6). Full curve a is based on the experimental data of Freyland (Ref. 2), and dashed curve b indicates the Curie limit for free spins. The critical density is 0.379 g cm^{-3} (Ref. 7).

The starting point of the present description is the phenomenological treatment of a correlation-induced metal-insulator transition at absolute zero $T=0$, due to March, Suzuki, and Parrinello.[8] Following Suzuki,[9] these authors wrote the ground-state energy per atom of a half-filled band near to the metal-insulator transition (in the metallic phase) as an expansion in the magnetization per atom m and the quasiparticle renormalization factor q. The latter is the discontinuity in the single-particle occupation number at the Fermi surface, which decreases continuously to zero at the transition. Thus

$$E(m,q)=E_0+am^2+\cdots +bq+cq^2+\cdots+eqm^2+\cdots \ . \tag{1}$$

The volume magnetic susceptibility χ is then

$$\chi=\frac{n_0\mu_0\mu_B^2}{2(a+eq)} \ , \tag{2}$$

where n_0 is the number density. Hence if a is zero, or vanishes at least as fast as q on approaching the transition, the susceptibility is enhanced, as in the Brinkman-Rice model[10] for such a system. For that particular case, we may readily identify the coefficients in the expansion (1), and find $a=0$, $b=(U_c-U)/8$, $c=U/32$, and $e=[1+\frac{3}{2}\bar{\varepsilon}N(\varepsilon_F)]/2N(\varepsilon_F)$, giving $\chi\sim q^{-1}$ as the authors originally noted. Here U is the Hubbard onsite interaction, $N(\varepsilon_F)$ is the electronic density of states per atom at the Fermi energy, U_c is the value of U at the metal-insulator transition, and $\bar{\varepsilon}$ is the band energy in absence of correlation.

Let us consider next the situation for $T\neq0$. A natural extension of Eq. (2) writes the free energy per atom at temperature T as

$$F(m,q,T)=E_0+a(T)m^2+\cdots+b(T)q +c(T)q^2+\cdots+e(T)qm^2+\cdots \ . \tag{3}$$

Here, of course, the interpretation of q in terms of the average number of doubly occupied sites (given explicitly in the Brinkman-Rice model) is more appropriate, since the discontinuity in the single-particle occupation number will not be such a well-defined quantity. Furthermore, as $T\rightarrow\infty$, we expect a reversion to Curie-like behavior in the susceptibility, as the degeneracy temperature of the

Fermi fluid is exceeded. This is achieved if the coefficient a in Eq. (3) is proportional to T, with the coefficient e much less strongly dependent on T, and remaining finite as $T\to 0$. Thus if $a=\alpha T$, then as $T\to\infty$, $\chi\to n_0\mu_0\mu_B^2/2\alpha T$, and for lower temperatures χ is always less than this limiting value, for all densities. If $\alpha=\frac{1}{2}k_B$, this is simply the Curie law for the electrons. As $T\to 0$ we have $\chi\to n_0\mu_0\mu_B^2/2eq$, and require $1/2e\to N(\varepsilon_F)$ in the limit of high density ($q\to 1$), if we are to regain the Pauli susceptibility. Thus we expect a gradual transition between these limiting behaviors, when $a\approx eq$, i.e., $2eq\approx k_BT$.

To proceed further, we draw upon the work of Rice, Ueda, Ott, and Rudigier,[11] who extended the original Brinkman-Rice model to finite temperatures, in order to describe the normal-state properties of heavy-electron systems. For a half-filled band, they wrote the free energy per atom as

$$F=\sum_{\mathbf{k}\sigma}q_\sigma\varepsilon_{\mathbf{k}}n_{\mathbf{k}\sigma}+Ud+k_BT\sum_{\mathbf{k}\sigma}w_{\mathbf{k}}[n_{\mathbf{k}\sigma}\ln n_{\mathbf{k}\sigma}+(1-n_{\mathbf{k}\sigma})\ln(1-n_{\mathbf{k}\sigma})]\ , \tag{4}$$

where $n_{\mathbf{k}\sigma}=\{1+\exp[q(\varepsilon_{\mathbf{k}}-\mu)/w_{\mathbf{k}}k_BT]\}^{-1}$, $w_{\mathbf{k}}$ is a renormalization factor in $\mathbf{k}$ space, introduced to account for the nonorthogonality of the quasiparticle states $n_{\mathbf{k}\sigma}$, and d is the average number of doubly occupied sites. Although clearly the details of $w_{\mathbf{k}}$ are not known, the constraints

$$\bar{w}=\sum_{\mathbf{k}}w_{\mathbf{k}}=[(\tfrac{1}{2}-d)\ln(\tfrac{1}{2}-d)+d\ln 2]/\ln 2\ , \tag{5}$$

$$\bar{w}_{-1}=\sum_{\mathbf{k}}w_{\mathbf{k}}^{-1}=2\ , \tag{6}$$

$$w\to 1 \text{ as } k\to k_f\ , \tag{7}$$

hold for the situation considered here. With

$$q=\{[d(n_\uparrow-d)]^{1/2}+[d(n_\downarrow-d)]^{1/2}\}^2/n_\uparrow n_\downarrow\ , \tag{8}$$

the magnetic susceptibility may be obtained by expanding the free energy to $O(m^2)$:

$$\frac{n_0\mu_0\mu_B^2}{\chi}=2q\left[1-\frac{1}{4(1-2d)^2}\right]\sum_{\mathbf{k},\sigma}\varepsilon_{\mathbf{k}}n_{\mathbf{k}\sigma}+k_BT\left[\sum_{\mathbf{k},\sigma}w_{\mathbf{k}}^{-1}n_{\mathbf{k}\sigma}(1-n_{\mathbf{k}\sigma})\right]^{-1}\ . \tag{9}$$

Now as $T\to 0$, the second term becomes $q/N(\varepsilon_f)$, and writing $\bar{\varepsilon}=\sum_{\mathbf{k}\sigma}\varepsilon_{\mathbf{k}}n_{\mathbf{k}\sigma}$ in this limit, then

$$\chi=\frac{n_0\mu_0\mu_B^2N(\varepsilon_f)}{q}\left[1+2\bar{\varepsilon}N(\varepsilon_f)\left[1-\frac{1}{4(1-2d)^2}\right]\right]^{-1}\ , \tag{10}$$

regaining the Brinkman-Rice result.[10] For $k_BT\gg q\varepsilon_f$, then $n_{\mathbf{k}\sigma}\approx\frac{1}{2}$, so that

$$\chi=\frac{n_0\mu_0\mu_B^2}{k_BT}\ , \tag{11}$$

using the value for $\bar{w}_{-1}$ from Eq. (6). Hence there is a crossover between enhanced Pauli paramagnetism and Curie behavior, for $k_BT\approx q\varepsilon_f$, and the structure of the theory is as suggested earlier in the phenomenological description. We may also note that for the low-temperature, high-density region of Fig. 1, Eq. (10) provides a mechanism for the observed enhancement of the susceptibility over the Pauli value and thus the upturn in the curve. Here, we may assume that the reduction of d from its uncorrelated value of $\frac{1}{4}$ is small. Writing $d=\frac{1}{4}-\delta$, where δ is small and positive, we find from Eq. (8) that $q=1$ to $O(\delta)$, and on expanding the bracket in Eq. (10) similarly, we obtain

$$\chi=\frac{n_0\mu_0\mu_B^2N(\varepsilon_F)}{1+16\bar{\varepsilon}N(\varepsilon_F)\delta}\ . \tag{12}$$

Since $\bar{\varepsilon}<0$, χ shows a Stoner-like enhancement, the effect of which will tend to diminish as the density falls, while at the same time the $1/q$ factor becomes more important.

Referring to Fig. 1, then at the maximum in the susceptibility curve, as Warren[5] pointed out, the enhanced Pauli susceptibility appears to be restricted by the Curie limit. At this point, $\rho\approx 0.8$ g cm^{-3} and $T\approx 1780$ K, giving $q\approx 0.18$ (i.e., $d\approx 0.02$). Thus the renormalization of the electron degeneracy temperature due to the effects of correlation is strongly marked. More generally, we will expect a crossover region in the behavior of the susceptibility to the high-density side of the metal-insulator transition, as indicated schematically in Fig. 2. The experimental data for rubidium and sodium,[3,4] which do not show a maximum like those for cesium,[2] do not extend to low enough densities for this to be seen, although we should expect them to before the metal-insulator transition is reached. We note, of course, that near to the liquid-vapor critical region, the susceptibility is likely to be subject to diamagnetic corrections, arising from the presence of aggregate species.

In summary, it is shown that the magnetic-

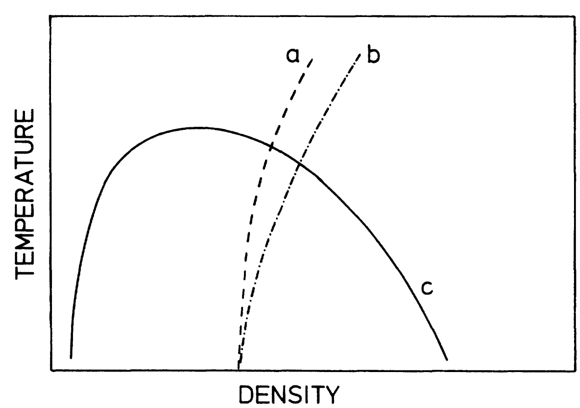

FIG. 2. Schematic representation of the relationship between the metal-insulator transition ($q=0$, labeled a), the crossover in the behavior of the magnetic susceptibility ($q\varepsilon_F=k_BT$, labeled b), and the liquid-vapor coexistence curve (labeled c).

susceptibility data on expanded fluid cesium can be interpreted by means of a phenomenological treatment, developed from that given by March, Suzuki, and Parrinello[8] for $T=0$. This is supported, at a microscopic level, by adapting the work of Rice *et al.*[11] on heavy-electron systems. If the peak in the susceptibility-density plot for cesium along the coexistence curve is interpreted as the limitation of enhanced Pauli behavior and consequent crossover to a Curie-like regime, then q at this point is ≈ 0.18. This figure constitutes an upper bound for the value of q at the metal-insulator transition, and it is of interest here to note the marked difference in behavior from the jellium model. There, $q \approx 0.53$ at the corresponding density,[12] and the metal-insulator transition occurs at a much lower density.[13] It is evident that the influence of electron-ion interaction in the real system is substantial.

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