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Magnetic susceptibility of metallic and nonmetallic expanded fluid cesium

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In this paper the first magnetic-susceptibility results for a fluid metal are reported, which cover a wide range of expansion between the normal melting point and conditions near the critical point. Measurements have been performed for fluid Cs at saturation conditions up to 1680 °C and 98 bar, that is 70°C below the critical temperature. In the expanded liquid state, the mass susceptibility first decreases slightly, followed by a strong rise with increasing expansion by almost a factor of 5. A pronounced paramagnetic maximum is observed near 1600 °C, corresponding to about double the critical density and a dc conductivity of about $10^3\ \Omega^{-1}\,\mathrm{cm}^{-1}$ This susceptibility enhancement indicates that the metal-nonmetal transition in fluid Cs might be of the Mott-Hubbard type. In the nonmetallic-dense-vapor phase, the susceptibility data give direct evidence for the existence of a high amount of diamagnetic molecular associations, like Cs_2 molecules.

I. INTRODUCTION

In fluid metals a metal-nonmetal transition (*M-N*) can be continuously studied by an expansion of the liquid up to supercritical conditions. Transformations of this type have been investigated in some detail for fluid Hg and, comparatively less extensively, for the expanded liquid alkali metals.[1] All the experimental observations in theses systems have shown one common feature, concerning the variation of the electronic properties in the transition region: from measurements of the dc conductivity,[2–4] thermopower,[5,6] Hall coefficient,[7] Knight shift,[8] and optical reflectivity[9]—the last two quantities have been measured only for fluid Hg—pronounced changes of both the density and temperature dependence of these quantities were found, whenever the conductivity decreased from about 10^3 to $10^2\ \Omega^{-1}\,\mathrm{cm}^{-1}$. As for the observed behavior of the electronic transport properties, these can be described quantitatively within the nearly-free-electron model,[10,11] as long as the mean free path of the conduction electrons is larger than the mean interatomic distance,[12] which corresponds to conductivities above about $10^3\ \Omega^{-1}\,\mathrm{cm}^{-1}$. Below about $10^2\ \Omega^{-1}\,\mathrm{cm}^{-1}$, a value estimated by Mott[13] as the minimum metallic conductivity, typical semiconducting characteristics have been found.[5] Concerning the region in the phase diagram, where the *M-N* transition occurs, a striking difference exists between the alkali metals and divalent Hg. Whereas in Hg the transition occurs at a density lying between the triple point and the critical-point density ρ_c, approximately at 1.6 ρ_c,[1] recent simultaneous measurements of *PVT* data and electrical transport properties directly indicate that in the case of the alkali metals the *M-N* transition is connected with the gas-liquid critical point.[14].

In the discussion of *M-N* transitions in condensed matter, systems of one-electron atoms have attracted special interest in recent years.[13] In particular, the question of the nature of the transition which dominates in disordered systems of this kind, is of central importance. Starting from the metallic side of the transition, different mechanisms are considered in parallel.[13] One model, cited often as a Mott-Hubbard transition,[13] emphasizes the intra-atomic electron-electron interaction, which at a reduced number density may lead to a splitting of the conduction band into two Hubbard bands. As a consequence, the electrical transport should be thermally activated at high temperatures. From calculations of Brinkman and Rice[15] it is suggested, that the Hubbard mechanism causes a great enhancement of both the Pauli paramagnetism and the electronic specific heat. If disorder plays an important role in expanded fluid metals, an additional phenomenon has to be considered. If the density of states for some energy interval is small, a localization of these states by disorder may take place. This phenomenon is commonly described by an "Anderson localization" (see, e.g., Ref. 12). As has been pointed out by Mott,[13,36] the density of states at the Fermi level, $N(E_F)$, might be reduced during the expansion of a fluid metal. In this way a pseudogap might form, where states around E_F might become localized in the Anderson sense.

For a theoretical treatment of these questions, fluid alkali metals may be considered ideal model substances, mainly for two reasons. The conduction band is a half-filled *s*-band made from one-electron centers, and the change from metallic to nonmetallic states may be followed by a simple variation in the number density. From an experimental point of view the situation is somewhat complicated, as conditions of high temperatues and pressures have to be achieved. This influences the experimental possibilities. Among the alkali metals the element with the lowest critical temperature and pressure is Cs, having $T_c = 1750\,^\circ\mathrm{C}$ and $p_c = 110$ bar.

The experimental data on fluid alkali metals which are available so far, give no direct insight into the problems discussed above. Magnetic properties, however, may show a distinct behavior as a function of density and temperature, depending on the type of interaction, which dominates the change from metallic to nonmetallic states. Therefore, we measured the magnetic susceptibility of fluid Cs for both the expanded liquid and dense vapor phase. The main objective of this work was to get possibly a direct experimental information with respect to the above questions. According to the technique applied, measurements have been performed under saturation conditions along the liquid-gas coexistence curve. It is the first time, that susceptibility results are reported for a fluid metal covering a wide range of expansion between the melting point and conditions near the critical point.

II. EXPERIMENTAL DETAILS AND RESULTS

The magnetic susceptibility was determined by the Faraday method. Special liquid containers had to be constructed which could withstand an internal overpressure up to 110 bar at temperatures near 1750 °C. These small pressure vessels were built from tungsten-rhenium alloys and were vacuum sealed tightly by a niobium cone fitting. The rough dimensions were 11 mm outside diameter and 30 mm total length, with an internal volume of 1.45 or 1.6 cm^3. In order to get reproducible results on heating and cooling and for subsequent runs with the same sample cell, measurements under high-vacuum conditions proved to be necessary. In this way we were sure that light oxygen films on the outside of the container were completely removed, which otherwise gave relatively large irreproducible paramagnetic signals. Therefore a high-temperature—high-vacuum molybdenum furnace was used in connection with a Cahn R100 microbalance. The furnace fitted inside a 63 mm magnet gap of gradient pole pieces, which allowed a maximum-field—field-gradient product, $H(dH/dz)$, of $8.66 \times 10^6\ \mathrm{G}^2\mathrm{cm}^{-1}$. This product changed by less than 4% over a vertical distance of ± 15 mm, which was calibrated with different small metallic samples. The reproducibility of the field setting itself was controlled by a small Hall probe to better ± 1 G.

The experimental procedure was as follows. Inside an argon glove box Cs of 99.95% purity was filled into the sample cell, which was closed under vacuum with the niobium cone. The amount of Cs, weighted with an accuracy of ± 0.5 mg, was chosen such that at the maximum measuring temperatures, the Cs never passed into the homogeneous liquid phase. Otherwise a steep pressure rise would have occured on further heating. After the measurements on the Cs samples, which were performed at different magnetic fields, the susceptibilities of the corresponding empty cells were determined in the same way as a function of temperature in separate runs. The difference of these two runs yielded the Cs susceptibilities. Special care was taken each time to hang the cell within ±0.01 mm at the same position inside the magnet gap, so that the force measurement on the same sample cell could be reproduced with an accuracy of $\pm 10^{-2}$ dyn. From the total measured susceptibility of Cs the contributions of the coexisting liquid and vapor phases were separated taking the data of several experiments with different Cs fillings. For this evaluation the weight fractions of liquid and gas were calculated with the saturation densities from different sources in the literature which were critically averaged.[14,16–19]

The temperature was measured by two W-Re thermocouples at different positions relative to the cell. A separate temperature determination was possible with the aid of a two color pyrometer, which was directly focused on the bottom end of the tungsten-rhenium cell. The maximum discrepancy between the different temperature indications above 1200 °C was $\lesssim 25\,^\circ\mathrm{C}$. So the temperature uncertainty is one of the main error sources in the susceptibility results. Further errors are due to the inaccuracy of the field-gradient profile, the empty cell corrections, and the determination of the weight fractions of the liquid and gas from the saturation densities. This last uncertainty is the main error contribution for the vapor susceptibilities at lower temperatures. Altogether a maximum absolute error for both the liquid and vapor susceptibilities of about ±10% is estimated for the higher temperatures.

In Fig. 1 the mass susceptibility, κ_g, of expanded liquid Cs is shown as a function of saturation temperature. The results plotted here were obtained from five experimental runs with different Cs fillings, which are indicated in the caption of Fig. 1 by the corresponding Cs masses. Between the melting point and about 800 °C, κ_g decreases slightly from 0.23×10^{-6} to $0.16 \times 10^{-6}\ \mathrm{cm}^3\mathrm{g}^{-1}$. The agreement of our result at the melting point with the Collings value[20] of $0.22 \times 10^{-6}\ \mathrm{cm}^3 g^{-1}$ is satisfactory. A striking change of κ_g occurs above 800 °C, where it increases by almost a factor of 5 up to 1600 °C, followed by a steep decrease for temperatures approaching the critical point. The susceptibility values at the highest temperatures contain only a small correction for the vapor phase, as under these conditions the sample cell was almost completely filled with liquid Cs.

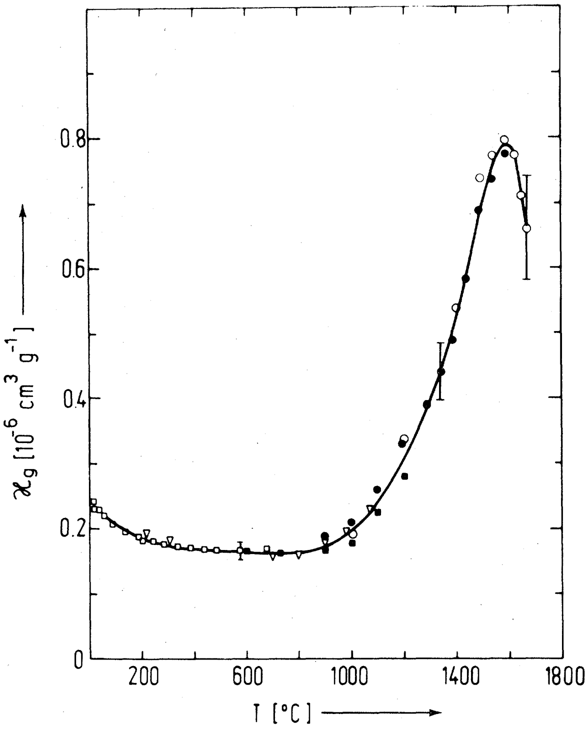

FIG. 1. Mass susceptibility κ_g of expanded liquid Cs vs saturation temperature. The experimental points correspond to separate measurements with different Cs fillings of 2.131 g (□), 0.869 g (▽), 0.825 g (■), 0.726 g (●), and 0.645 g (○).

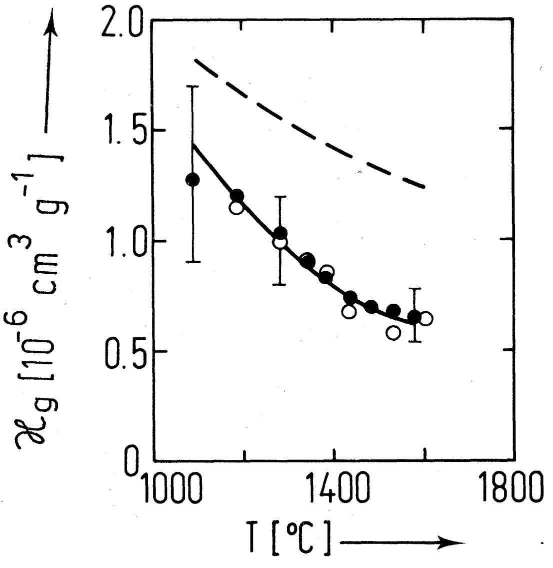

FIG. 2. Mass susceptibility κ_g of saturated dense Cs vapor. Experimental data correspond to Cs fillings of 0.1397 g (●) and 0.234 g (○), respectively. For comparison the theoretical Curie behavior of a monatomic Cs gas, see the discussion, is drawn as a dashed line.

The susceptibilities for the dense vapor phase at saturation conditions are plotted in Fig. 2 versus temperature. The relativitely large error bars at low temperatures correspond to the uncertainty in the determination of the weight fraction of vapor at low densities. Compared with the theoretical behavior for a monatomic Cs vapor of Curie-type paramagnetism, drawn as a dashed line in Fig. 2, a clear diamagnetic deviation of the experimental results is observed, increasing with temperature and density. Problems with temperature stability above 1680 °C and with pressure resistance of the sample cells above 100 bar at these temperatures do not yet allow us to extend the measurements up to the critical point. Especially near the critical point a high temperature accuracy is needed, as the density strongly varies with temperature.

III. DISCUSSION

In the metallic regime at high densities we may assume, that the change of κ_g is mainly caused by the expansion of the liquid. However, for a more quantitative comparison with the predictions of different models the separate influence of temperature has to be taken into account. In order to get a view of the overall change of the susceptibility going from the metallic to the nonmetallic phase, the interesting discussion at first is that as a function of density. Therefore, both the liquid and vapor susceptibilities are plotted versus saturation density in Fig. 3, together with some σ values at saturation conditions (upper scale). An interesting observation of this plot is, that the maximum in κ_g at $\rho \approx 0.8$ g cm^{-3} coincides with a conductivity value $\sigma \approx 10^3$ Ω^{-1} cm^{-1}. Obviously the magnetic interaction goes through a maximum, when the electronic transport ceases to be nearly free electron like. Extrapolating κ_g from both sides to the critical density ρ_c it seems, that a minimum in κ_g appears near the minimum metallic conductivity of about 10^2 $\Omega - 1$ cm^{-1}. This minimum might be less pronounced if one could plot κ_g versus density at constant temperature. However, in any case a paramagnetic increase will occur with reducing density in the dense vapor phase, as with reducing pressure the chemical equilibrium is shifted towards paramagnetic species, which is discussed below. The rapid increase of paramagnetism at very low densities in the left-hand portion of Fig. 3 is of course determined by the Curie-law temperature dependence of atomic Cs along the vapor branch of the coexistence curve.

For a more detailed discussion of the correlation between the *M-N* transition and the change in the magnetic interaction a knowledge of the electronic paramagnetism alone is important. For this aim we use the same procedure which Dupree and Seymour[21]

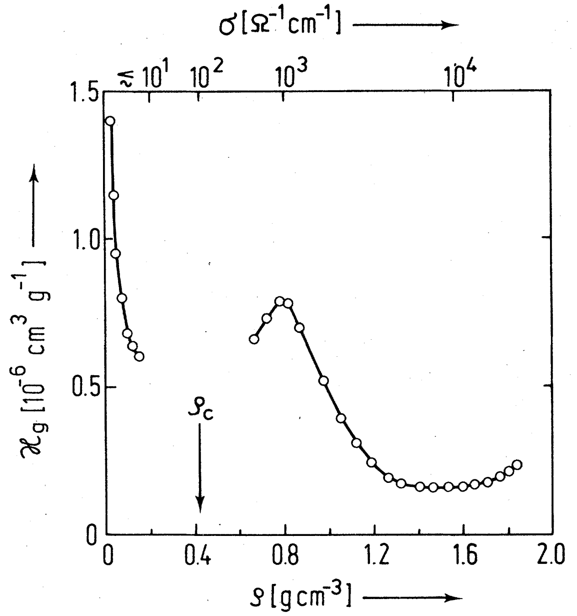

FIG. 3. Liquid and vapor susceptibility of Cs vs saturation density. The plotted points have been averaged from the results of Fig. 1 and 2. The density data have been taken from Refs. 14 and 16–19. The conductivity values σ on the upper scale are based on the results of Refs. 3, 6, 14 and 19. The critical density is given as $\rho_c = 0.42$ g cm^{-3}.

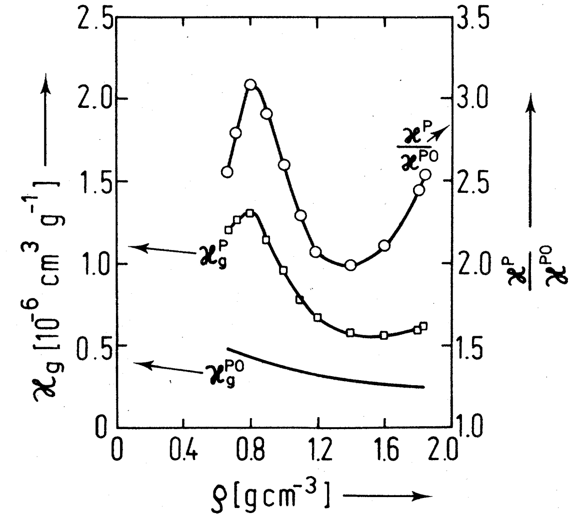

FIG. 4. Density dependence of the paramagnetic susceptibility of conduction electrons, κ_g^p, and of the free-electron Pauli susceptibility, κ_g^{p0}, of expanded liquid Cs. The enhancement factor, κ^p/κ^{p0}, is drawn by open circles and is given on the right-hand scale.

applied to a number of liquid metals, getting results in good agreement with the directly measured values of conduction-electron-spin resonance. We start with a division of the liquid susceptibility κ into three components

$$\kappa = \kappa^i + \kappa^d + \kappa^p \ , \qquad (1)$$

where κ^i is the susceptibility of the ion cores, κ^d the orbital diamagnetism of the conduction electrons, and κ^p the conduction-electron paramagnetism. As a first approximation, κ^i should remain constant over the whole of the metallic range, and so the molar[22] value for the Cs$^+$ ion of $\kappa_m^i \approx -35 \times 10^{-6}$ cm^3 mole^{-1} is taken from the literature (κ_g denotes mass susceptibilities, κ_m molar susceptibilities). For a free-electron gas, κ^d is given by the well-known Landau diagmagnetic term. However, by the effect of electron-electron interaction it should be increased as has been shown in a number of calculations. We took this enhancement into account, which is a small correction compared with the resulting κ^p values, using the theoretical results of Kanazawa and Matsudawa[23]

$$\kappa^d = \kappa^{d0}[1 + 0.0276 \cdot r_s(\ln r_s + 1.51)] \ . \qquad (2)$$

Here r_s is the electron radius in atomic units and κ^{d0} denotes the Landau susceptibility of free electrons. With these input data, κ^p of expanded Cs has been determined from the liquid susceptibility. Figure 4 shows this result in comparison with the free-electron Pauli susceptibility, κ^{p0}, which has a weak density dependence for the mass susceptibility of $\kappa_g^{p0} \propto \rho^{-2/3}$. Also included in Fig. 4 is the paramagnetic enhancement factor, κ^p/κ^{p0}, given on the right-hand scale.

From this presentation, two distinct mechanisms for the susceptibility enhancement may be concluded. First, there is a relatively high enhancement of about 2.5 near the melting point, which decreases to a minimum of about 2 with reducing the density. An enhancement of the order of 1.2 to 1.5 is typical for most normal liquid metals at their respective melting points, the trend going to higher values with increasing atomic number.[21] In the group of the alkali metals the enhancement is exceptionally large being about 1.6 for Na,[21] and reaching about 2.5 for Cs. On melting, only small changes of several percent are found.

Many theoretical papers have dealt with the spin-susceptibility enhancement of metals, incorporating exchange-correlation effects, see, e.g. the reviews by Hedin and Lundquist[24] and Herring.[25] The most recent calculations of this problem by Vosko *et al.*[26] and Moruzzi *et al.*[27] find a relatively good quantitative agreement with the observed enhancement factors of metals and particularly of the alkali metals. The expression given by Moruzzi, Janak, and Williams[27] for the susceptibility enhancement is

$$\frac{\kappa^p}{\kappa^{p0}} = \frac{1}{1 - JN(E_F)} \ , \qquad (3)$$

where J is the exchange-correlation integral. On the basis of this dependence of κ^p on J, a probable explanation of the decrease of κ^p/κ^{p0} found in this work is, that with increasing expansion of the liquid the exchange-correlation integral is reduced. It is interesting to note at this point, that the first susceptibility results of Rb show a very similar trend.[28] However, the reduction of κ^p/κ^{p0} with decreasing density is weaker and the minimum of $\kappa^p/\kappa^{p0} \approx 1.83$ for Rb is shifted nearer to the melting point compared with Cs. This is surely related to the smaller enhancement of Rb at the melting point itself, being 1.94.[28] On the other hand, it is interesting to note, that the density dependence of the susceptibility enhancement of the present results near the melting point is opposite to that inferred from studies of liquid-alkali-metal alloys[29] for $5.2 < r_s < 5.8$.

If the above interpretation is valid at high liquid densities, then a second, distinct interaction must be responsible for the strong increase of the enhancement factor at the lower liquid densities, which is of similar steepness in expanded liquid Rb.[28] Considering only the intra-atomic electron correlation, Hubbard model, the calculations of Brinkman and Rice[15] predict a susceptibility enhancement of the following form:

$$\frac{\kappa^p}{\kappa^{p0}} \propto \left[1 - \left(\frac{U}{C_0}\right)^2\right]^{-1} \qquad (4)$$

Here U is the intra-atomic Coulomb repulsion and C_0 is proportional to the average energy without correlation. Applying this expression to an expanded liquid metal one should expect a high enhancement, as on decreasing the density, U should increase and C_0 should be reduced in proportion to the narrowing of the bandwidth (for this point we refer to the detailed analysis by Mott[13]). According to a rough estimate given by Mott,[13] the maximum enhancement near the magnetic transition should be about $z+1$, where z is the coordination number. Now, recent neutron-diffraction experiments on expanded fluid rubidium have shown that during the expansion of a liquid metal between the melting point and the critical point, the nearest-neighbor distance changes only a little, whereas the average number of nearest neighbors decreases linearly with the density.[30] So, for liquid Cs at $\rho \approx 0.8\ \mathrm{g\,cm^{-3}}$ a value of $z \approx 4$ may be assumed, yielding a maximum enhancement factor for the highly correlated electron gas of about 5. This lies in the right order of magnitude of the experimentally observed value of 3.1. However, in comparing these two numbers, it must be pointed out critically, that all these considerations do not contain the separate influence of temperature, which may not be neglected.

In their paper on the metal-insulator transition, Brinkman and Rice[15] "speculate, that the correlation effects could possibly lead to a first-order transition between a paramagnetic metallic state and an antiferromagnetic insulating state." Now, in fluid nonmetallic Cs only short-range order persists and the atomic centers are mobile, so that the natural analogy of an antiferromagnetic ordering in the solid state should be a spin pairing of nearest-neighbor centers resulting in the formation of molecules. This again, leads to a state of lower energy. In fact, the magnitude of the total vapor susceptibility is consistent with existence of a relatively high amount of Cs_2 molecules. In order to put this in a more quantitative way, we consider a simple chemical equilibrium of monatomic Cs and diatomic Cs_2, and split the total vapor susceptibilities into two contributions:

$$\kappa_g = \frac{1}{\bar{M}}\left[(1 - X_{Cs_2})\kappa_m^{Cs} + X_{Cs_2}\kappa_m^{Cs_2}\right] \ . \qquad (5)$$

Here κ_g is the mass susceptibility of the vapor, $\bar{M}$ the average molecular weight, κ_m^{Cs} the molar susceptibility of atomic Cs, $\kappa_m^{Cs_2}$ that of diatomic Cs_2, and X_{Cs_2} is the mole fraction Cs_2. The susceptibility of Cs is composed of the spin paramagnetism of the 6s-electron and a diamagnetic part, which may be approximated by that of the Cs^+-ions

$$\kappa_m^{Cs} = \frac{N_L \mu_B^2}{kT} - 35 \times 10^{-6}\,\mathrm{cm^3\,mole^{-1}} \ . \qquad (6)$$

The Cs_2 molecules in the ground state contribute only a diamagnetic term, and we took

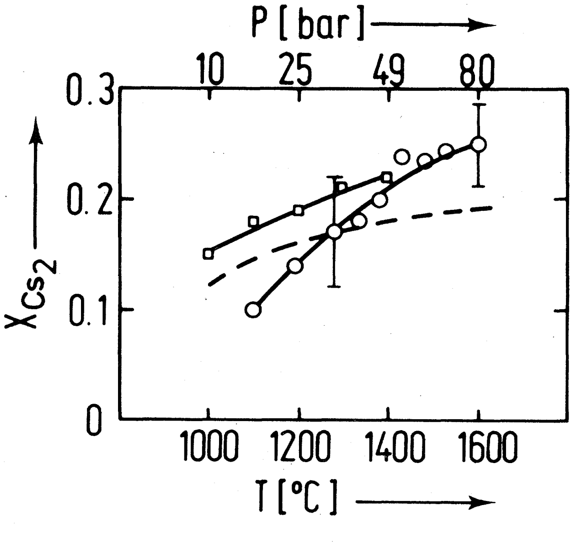

FIG. 5. Mole fraction of Cs_2 molecules, X_{Cs_2}, of the nonmetallic dense Cs vapor (the temperatures and pressures belong to the coexistence curve). Points marked by circles (○) have been derived from the susceptibilities of this work, the squares (□) are from Ref. 32. The dashed curve has been calculated with statistical mechanics for the ideal-gas equilibrium $2Cs \leftrightarrow Cs_2$. The molecular data for this calculation have been taken from Refs. 33 and 34.

$\kappa_m^{Cs_2} \approx -100 \times 10^{-6}$ cm^3 mole^{-1}, which seems a reasonable value in comparison, for instance, with -90×10^{-6} cm^3 mole^{-1} for the I_2 molecule.[22] The result of this calculation of X_{Cs_2} is shown in Fig. 5 versus temperature and pressure, respectively. The observed increase of X_{Cs_2} with increasing pressure is not surprising, this is just what one should expect for this simple thermodynamic equilibrium. In Fig. 5, data are compared with a statistical thermodynamic calculation for independent particles,[31] drawn as a dashed curve, and with the results of Ewing *et al.*, which have been derived from a quasichemical study of *PVT* data.[32]

In this evaluation of the vapor susceptibilities, no allowance has been made for the occurence of higher molecular associations, which should exist to some degree[32] or for the ionization of Cs_2 molecules. For an ideal gas of Cs_2 molecules, one estimates an ionization degree of about 10^{-4} at 1600 °C, taking 3.2 eV for the ionization potential of the molecule.[34] However, with increasing vapor density the ionization energy of the molecule will be reduced, so that much higher ionization degrees should be expected.[35] This, on the other hand, would result in the more stable molecular species of Cs_2^+,[34] and possibly in the occurence of ionized higher molecular associations.

From the susceptibility alone, all these different species cannot be deduced. However, they should become important if the critical point is approached from the nonmetallic vapor side. In the intermediate density range between the critical density and 0.8g cm^{-3} the dc conductivity changes from about 10^2 to 10^3 Ω^{-1} cm^{-1}. If the transport in this regime is diffusive and a pseudogap opens, as has been first suggested by Mott,[36] then the strong decrease of κ^p/κ^{p0} below 0.8 g cm^{-3} may be a direct indication of a reduction in $N(E_F)$. This interpretation of the decrease of κ_p below the Brinkman-Rice enhancement would imply, that with increasing disorder near the critical point the system undergoes a second transition for conductivity of the Anderson-type. The possibility, that within the Hubbard model a magnetic transition might occur before the two Hubbard bands separate, has been the subject of several theoretical papers[37] and is discussed in some detail in the Mott book on the metal-nonmetal transition.

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