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Metallic-Nonmetallic Phase Coexistence above the Consolute Point of Sodium-Ammonia Solution

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The heat capacity under saturated vapors, C_σ, of three different concentrations of Na-NH_3 solution ($X = 0.045$, 0.046, 0.063 molar part of Na) has been measured in the temperature range 200–300 K. All three $C_\sigma(T)$ curves show anomalies consistent with the existence of a new two-phase region above the well-known liquid-liquid critical point ($X_c = 0.0415$, $T_c = 232$ K). Its location is compatible with the metal-nonmetal transition line; so it is believed that in equilibrium these are metallic and insulating phases with different concentrations of electrons.

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Although thermodynamics of metal-ammonia solutions have been studied intensively,[1] heat-capacity data have never been obtained because of experimental difficulties. Interest to heat-capacity data is connected with the investigation of singularity of thermodynamic potential in the vicinity of the critical (consolute) point of these solutions in presence of metal-insulator transition which is typical for them.[2]

We succeeded in measuring the heat capacity of three sodium-ammonia solutions ($X = 0.0450$; 0.0462, and 0.0631, all ± 0.0006 of molar part of metal) in the temperature range from 200 to 300 K with an adiabatic calorimeter. Our data gave us evidence of a new two-phase region above the well-known critical point just in the interval where metal-insulator transition takes place. This new fact has to be very stimulating especially for the interpretation of data and looking for new details in the extensive investigation of variety of ionic systems[3] and expanding metals exhibiting the analogous metal-insulator transition.[4]

Our calorimeter and its technique have been described before.[5] The solutions, prepared as usual by multiple vacuum distillation of sodium and ammonia and analyzed by conventional procedures, were filled in small pyrex glass containers which were placed in the calorimeter with proper coils and thermocouples. The glass containers could resist an inner pressure of up to ~10 bars, corresponding to the normal ammonia vapor pressure at room temperature. Their heat capacity was only 20% of that of the solution; it therefore does not affect the accuracy of our data. The error of the heat capacity obtained with the calorimeter does not exceed 0.2%. Additional scattering of data is observed only when the system is not in equilibrium. It happens when the time period be-

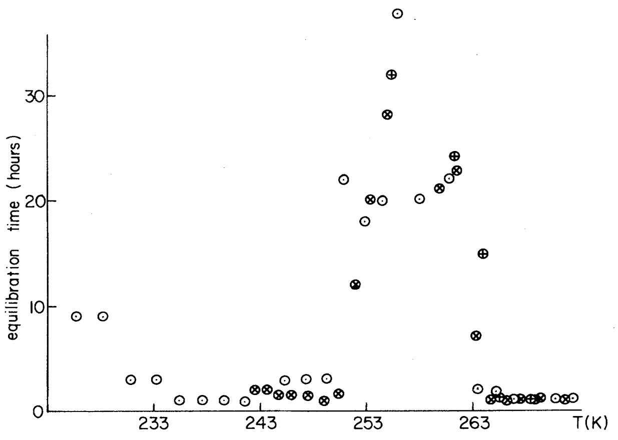

FIG. 1. Equilibration time τ as a function of temperature T for Na-NH_3 solution $X = 0.063$ Na.

tween electrical heating of the calorimeter and temperature reading is too short compared to an equilibration time of the sample.

In Fig. 1 the necessary equilibration time of one of our solutions ($X = 0.063$ Na) is plotted versus temperature. In the ranges from 233 to 251 K and from 263 K to the end of interval of our measurements the equilibration time is about one hour; normal heat conduction is the process for attaining equilibrium. But in interval between 251 and 263 K the equilibrium is achieved only after 10–20 h, indicating that slower processes are predominant. Equilibration times of this magnitude have been typically observed in two-phase liquid-liquid systems[5] where diffusion is time controlling (mean diffusion time $t = l^2/D \approx 10^5$ sec with the length l of our cell ~ 4 cm and the diffusion coefficient in the concentrated metal-ammonia solutions $D \approx 10^{-4}$ cm^2/sec). Thus an additional phase separation is probable in this interval above the long known miscibility gap below 232 K.[2]

C_σ/T curves of two samples are plotted in Fig. 2. We did not subtract the heat capacity of glass and copper of the calorimeter and container. So the heat capacity plotted in Fig. 2 is the total measured magnitude without corrections and any dependence on interpretation. The curves display discontinuities or jumps (about 1–2% of the absolute value, which is far beyond the uncertainty of the method) typical for crossing the border line of a miscibility gap. Thus the negative jump in curve *a* at lower temperature is the expected one due to the already known miscibility gap (Fig. 3). But the positive and negative jumps at higher temperatures (curves *a* and *b* in Fig. 2) where we observed the long equilibration times (see Fig. 1) definitely are connected to another phase insta-

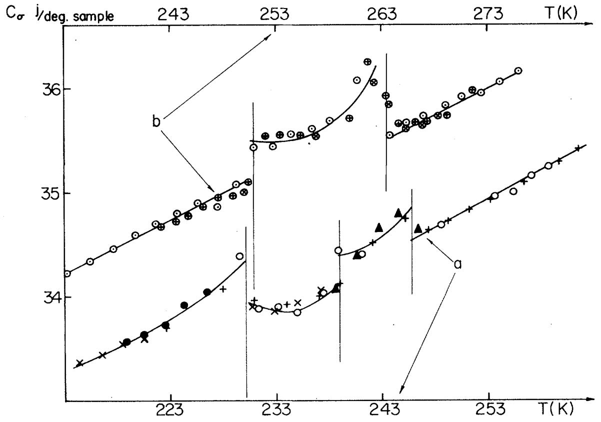

FIG. 2. Heat capacities under saturated vapor C_σ of two samples of Na-NH_3 solution. (a) $X_a = 0.046$ Na and (b) $X_b = 0.063$ Na. Different symbols denote the different runs of the experiment.

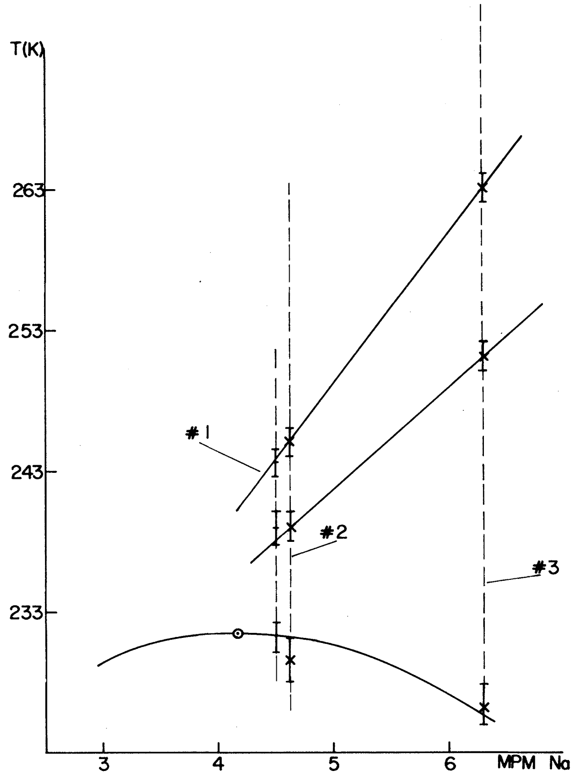

FIG. 3. Preliminary diagram of state of Na-NH_3 solution above its consolute point (dot in circle). Solid lines are coexistence border lines. We measure along dashed lines. Line nos. 1, 2, and 3 represent different samples with concentrations $X_1 = 0.045$, $X_2 = 0.046$, and $X_3 = 0.063$ Na, respectively.

bility, i.e., demixing of the system, which has not been observed before. These jumps are even more pronounced at higher temperature for the curve *b* of higher concentration ($X = 6.3\%$ Na) which is far enough from the miscibility gap mentioned before and critical point. One can see in Fig. 2 that curves *a* and *b* include points of different series measured during a long time. Because of the long equilibration time, it took from 10 to 100 h to get one experimental point and up to three months to get full curve for one sample. In spite of this long time period, less than 0.7% of the sodium have decomposed ($Na + NH_3 = NaNH_2 + \frac{1}{2}H_2$; the degree of decomposition was calculated from the amount of hydrogen collected after breaking the glass cell at the end of the experiment, when also the chemical analysis for sodium and ammonia were carried out) and heat capacity is highly reproducible along both curves.

The relatively large regular temperature dependence of C_σ in Fig. 2 is a result of evaporation of ammonia within the cell. This evaporation is a monotonous function of temperature and cannot reflect our main result.

Using the data of Fig. 2 (and of the curve for concentration $X = 4.5\%$ Na which looks similar to a—$X = 4.6\%$ Na) we may indicate this new region of instability as has been done schematically in Fig. 3. The location of this two-phase region is in qualitative agreement with the possible metal-nonmetal transition line[6] and the line of maximal correlation length[7] for Na-NH_3 and Na-ND_3 systems. Unfortunately the authors[7] did their neutron scattering observations at the critical concentration only. So their correlation length for any other concentration is just a result of a calculation from thermodynamic data.

The coexistence we have traced (Fig. 3) above the liquid-liquid critical point of the solution was predicted in very general terms by one of us.[8] This work gave us a general approach to an interpretation of our data. Indeed the main idea of Ref. 8 is that mass action law which determines numbers of ionized and neutral particles in such mixtures gives for them a multiple solution of equation of state. So the coexistence of two phases with different concentrations of electrons is possible irrespective of the usual (let us name it van der Waals) separation curve which is traditionally linked with the metal-nonmetal transition in this solution. The critical point of this new coexistence is connected only with Coulomb interaction [$T_{\text{Coulomb}} \simeq 520$ K (Ref. 8)] and is much higher than the well-known van der Waals ($T_c = 232$ K) critical point. It means that two phases in equilibrium that have been observed in our experiment are metallic and nonmetallic phases and the only difference between them is the concentration of electrons and cations.

The serious question arises why people did not observe this phase separation earlier. As one can see from Fig. 3 the width of this coexistence is considerably smaller than for the van der Waals coexistence. It means the density difference between phases is also small ($\sim 10^{-4}$–10^{-3} g/cm^3). But the temperature gradient of about 0.1–1 deg/cm produces the same order of density gradients in liquid ammonia in this temperature region. Since most of the investigations did not concentrate on achievement of better homogeneity of the temperature field and never expected the large equilibration times they had no chance to detect the phase separation in this part of T-X plane for metal-ammonia solutions.

The same reasons make a percolation of phases in this region very probable instead of a full separation of mixture. It might renew a validity of a percolation hypothesis[9] for the interpretation of experimental data in this field if other metallic solutes also exhibit the anomaly reported here.

The heat-capacity measurement is just one of the most relevant properties for such a complicated case because of an integral character of measurement procedure and differential character of the property sensitive to homogeneity of a system. We believe this is only a beginning of deeper investigation. Conductivities, ESR, and electromotive force measurements of alkali-metal–ammonia systems are in preparation.

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Effect of High Magnetic Fields on the Electronic Specific Heat in the Strongly Pauli-Paramagnetic Compound $LuCo_2$

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The low-temperature (1.3 to 20.0 K) heat capacity of the strongly Pauli-paramagnetic $LuCo_2$ compound was measured in magnetic fields up to ~10 T. The measured results show that the electronic–specific-heat constant decreases with increasing magnetic field (11% at 10 T), while the Debye temperature does not change. This is probably due to the depression of spin fluctuation enhancement of the heat capacity by moments induced on the cobalt atoms by the high magnetic fields. These results appear to be in accord with recent theoretical predictions.

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The anomalous enhancement of the electronic contribution to the heat capacity due to spin fluctuations in strongly Pauli-paramagnetic metals has been of considerable interest theoretically for about a decade.[1] Apparently only Brinkman and Engelsberg[2] have treated the problem of the effect of magnetic field on the enhanced electronic specific heat, and they suggested enormous magnetic fields are required to reduce the spin fluctuation enhancement to the specific heat. As far as we are aware no experimental evidence has been reported showing that an applied field reduced the enhancement due to spin fluctuations. Recently, however, we have found that the application of a magnetic field of ~10 T lowers the electronic-specific-heat constant of $LuCo_2$ by about 10%. The results of low-temperature (1.3 to 20 K) heat-capacity measurements as a function of magnetic field and the impact of these results on the theoretical models is described below.

For a nearly ferromagnetic metal the low-temperature heat capacity is given by

$$C=\gamma T+\beta T^3+cT^3\ln(T/T_s), \qquad (1)$$

where γT and βT^3 are, respectively, the usual electronic and lattice contributions to the heat capacity, and the third term on the right is the increase in the heat capacity due to spin fluctuations (paramagnon interactions).[1-4] The constant c includes the term $1/T_s{}^2$ where T_s is the characteristic spin fluctuation temperature. As shown by Lederer and Mills[5] and by Engelsberg, Brinkman, and Doniach,[6] Eq. (1) is valid only for the case of a uniform enhancement throughout the lattice, but if one takes into account local enhancement on one atom (the magnetically dilute solute atom) then the $T^3\ln T$ term is negligible except for $T<T_s/100$ and the next leading term is small and has a T^3 dependence. Subsequently many modifications and improvements have been made on the original models,[3-6] and these have been recently reviewed by Moriya.[1] However, most authors did not treat this problem as a function of magnetic field.

It was first pointed out by Brinkman and Engelsberg[2] and more recently by Hertel, Appel, and Fay[7] that the application of high magnetic fields offer at least one way of testing the spin fluctuation theory. Brinkman and Engelsberg explained that high magnetic fields of the order of characteristic spin fluctuation temperature, T_s, are required to quench the spin fluctuation enhancements. Hertel, Appel, and Fay,[7] who have made a more detailed mathematical analysis, suggest that if the Stoner enhancement and the mass enhancement due to spin fluctuations are large (~4 and ~1.5, respectively) and if the spin fluctuation temperature T_s is small (~15 K) a depression of the heat capacity of about 1% might be expected at 10 T. They have suggested an *f*-band metal such as UAl_2 might have the three parameters with the