Electron paramagnetic resonance in frozen solutions of sodium in ammonia

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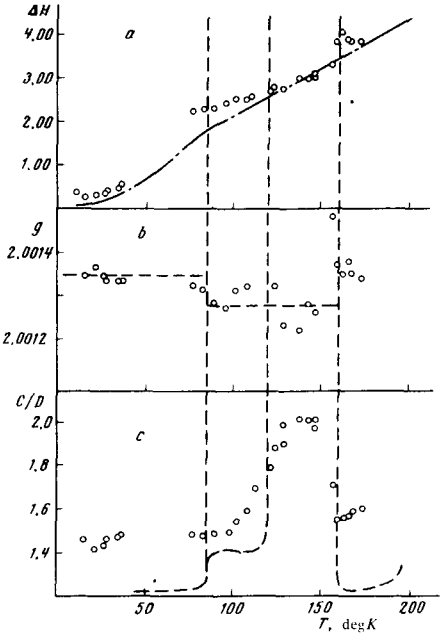
Preliminary experimental data are obtained on the g factor, width, and degree of asymmetry of the electron-paramagnetic-resonance line of rapidly frozen metal-ammonia solutions of sodium in the temperature interval 10–180 °K near concentrations ~3 at.%. A possible structure is suggested for the investigated systems.

Interest in the possible high-temperature superconductivity of frozen metal-ammonia solutions of sodium (MASS) has recently been renewed.[1–4] Although the first experiments in this direction were carried out by Ogg back in 1946,[5] there are still no reliable experimental data on the structure of this system, inasmuch as all the experiments were devoted principally to the electric conductivity of the samples.

We have undertaken a structure investigation of MASS by the electron paramagnetic resonance (EPR) method, without examining for the time being the physical nature of the anomalous electric conductivity.

The measurements were performed with a "B-ER 418s" stationary modulation radiometer in the 3-cm band. The samples were produced with commerical ammonia, which was first purified by preparing the intermediate MASS and subsequent partial evaporation of the ammonia. The purified ammonia was condensed in a volume-graduated glass test tube of 3 mm diameter, terminated by a measuring capillary of ~0.5 mm diameter and 30 mm length. After condensation, a batch of sodium (certified purity 99.9 wt.%) was added to the test tube to obtain the required solution concentration. We investigated concentrations in the range 2.5—3.8 at.%. The upper part of the test tube was filled with picein to prevent direct contact between the sample and the atmosphere. The "quenching" of the solution was in liquid nitrogen, after which the sample was rapidly transferred to a Dewar tube (inside the measuring resonator of the microwave spectrometer), in which the necessary temperature was established beforehand by blowing helium vapor. The EPR measurements were performed with rising temperature, both from the first quenching point (77 °K), and from the temperature of the second quenching in helium vapor (10 °K). The second quenching makes it possible, in our opinion, to stop the temporal evolution of the system and to fix the metastable structure of the MASS, so as to investigate it at lower temperatures. The time interval between the instant of the first quenching and the start of the EPR measurement was less than three minutes. Control measurements of the electric conductivity of a number of samples were made by a potentiometer method. They were in qualitative agreement with the data of[1].

The figure shows typical EPR measurement results for one of the MASS samples with concentration 3.2 at.%. The dashed lines show the data of[1] on the electric conductivity of rapidly quenched MASS. The curve "a" corresponds to a temperature dependence of the EPR linewidth. The dash-dot line shows the published data for metallic sodium.[6,7] Following a second slow cooling of the samples, the temperature dependence of the reciprocal of ΔH coincided with the curve for metallic sodium. Curve "b" shows the dependence of the g-factor on the temperature. We note that the available published data on the g factor for metallic sodium point to its independence of the temperature. The numerical values of g obtained by various authors differ by $\sim 10^{-4}$ ($g = 2.0013$).[6] Curve "c" shows the temperature dependence of the asymmetry parameter C/D of the resonance line, which characterizes the bulk electric conductivity of the sample and ranges from unity to 2 on going from the pure metal to the dielectric.[8] We point out that on this curve the transition from the conducting region to the dielectric one is smoother than in[1]. The data for the conducting region above 160 °K will not be discussed further, since the



Temperature dependence of the line parameters of EPR in MASS with concentration 3.2 at.%. The circles show our experimental results.

phase diagram of frozen MASS shows at $T \approx 100$ °K a highly concentrated liquid component, and the system becomes essentially two-phase.

The results suggest the following conclusions: Judging from the temperature dependence of the parameters of the EPR spectrum, the observed signal can be identified with paramagnetic resonant absorption by the conduction electrons in the metallic sodium, and is evidence of the presence of minute metal particles in the frozen MASS. At the same time, the numerical values of ΔH and $\partial \Delta H/\partial T$ differ somewhat from those of sodium, and the g factor on the boundary of the conducting and dielectric regions experiences a discontinuity $\Delta g \approx 5 \times 10^{-5}$. These two distinguishing features in the behavior of the resonance line definitely exceed the experimental error. The deviation of $\Delta H(T)$ can be understood by taking into account the spin relaxation of the conduction electrons on the surface of the metallic particle. It is necessary to assume here that up to ~80 °K the inelastic scattering of the spin from the surface yields a temperature-independent contribution to ΔH (surface relaxation of the Dyson type), and the decrease of the surface contribution to the width with increasing temperature above 80 °K is connected with a transition to a different type of relaxation ("diffusion" surface relaxation).[6] The proposed interpretation permits a rough estimate of the average metal-particle dimension. The contributions from the two types of surface relaxation can be satisfactorily reconciled at a particle diameter $\approx 0.5\ \mu$ and at an average probability of spin reorientation in the collision of the electron with the surface $\epsilon \approx 2 \times 10^{-6}$. A close value, $d \approx 0.2\ \mu$, is obtained from independent estimates of the particle dimension from the parameter C/D[8] in the dielectric region, with allowance for the size of the skin layer for sodium at the working frequency ~10^{10} Hz.

We can therefore assume on the basis of the obtained experimental data that the structure of the considered systems is a finely dispersed metallic sodium with average particle diameters 0.2–0.5, embedded in a medium of solid ammonium, or else of MASS with reduced concentration.

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