Proton relaxation in a solid solution of sodium in ammonia

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A deep minimum of the time T_1 of the NMR of the ammonia protons was observed in the dielectric region (near 150°K) of an electrically-conducting sodium-ammonia solution. Numerical estimates of T_1 and of the activation energy have confirmed the model wherein metallic sodium (in the form of a spiderweb) is present in the conducting region and the dissociation of the sodium atoms near 150°K.

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The observation of an anomalously high electric conductivity of a solution of several atomic percent of sodium in ammonia, rapidly, frozen ("quenched") at 77°K or below, has created so much interest, that the system was claimed to

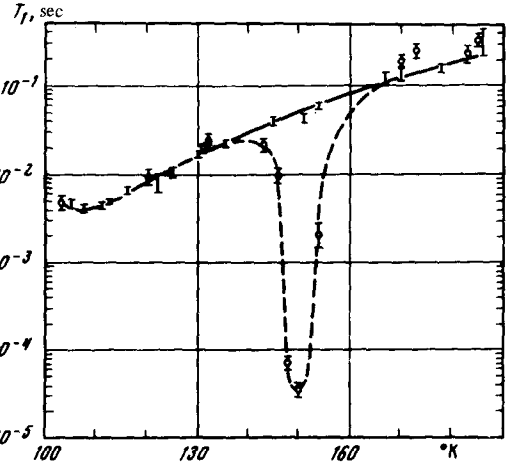

FIG. 1. Solid curve—time T_1 of pure ammonia according to the data of[2]; dashed—our measurements of a solution of 2.5 at.% Na.

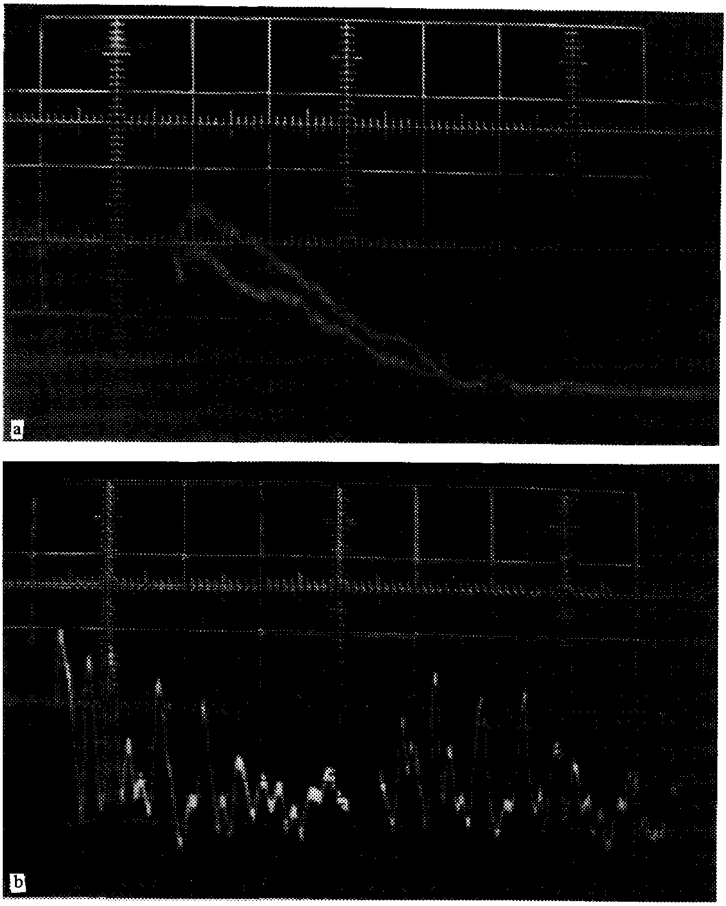

FIG. 2. Oscillograms of free induction signal: a) $T = 130\,^\circ$K, double exposure, interval between pulses $\tau = 0.5$ sec, sweep 5 μsec/cm; b) $T = 150\,^\circ$K, $\tau = 80$ μsec, sweep 20 μsec/cm.

have high-temperature superconductivity (for a comprehensive literature see[1]). Although careful measurements have revealed no anomalies in the conductivity in comparison with metallic bulk sodium,[1] the structure of the solution and its properties have remained a debatable question.

On the temperature dependence of the electric conductivity, interest attaches to the dielectric region near 150 °K, on both sides of which the conductivity is essentially "metallic."

Our NMR measurements of the relaxation of ammonia protons were carried out with the temperature raised from 100 to 180 °K. A sample, approximately 1 cm^3, was prepared by dissolving metallic sodium (enough to obtain a 2.5 at.% solution) in condensed commercial but dessicated (through a filter with KOH) ammonia, followed by freezing at liquid-nitrogen temperature. The measurements were made 4—5 h after the preparation of the sample, so that the resistivity was 1.5—2 orders of magnitude larger than the minimum value, but its time variation was stabilized.[1] The NMR frequency was $f_0 = 12.4$ MHz.

The results of the measurements of the spin-lattice relaxation times T_1 of the protons are shown in Fig. 1. The same figure shows a plot of $T_1(T)$ of the protons of pure (99.999%) ammonia at $f_0 = 10.8$ MHz from[2]. The small minimum at 106 °K is due to molecular rotation of the ammonia. Outside the region 140—160 °K, the pure NH_3 and the solution 2.5 at.% Na-NH_3 had the same times T_1. At 150 °K, a deep minimum is observed for the solution. The shapes of the free-induction signals (Fig. 2) are also peculiar: outside the minimum the curves are close to Gaussian, but near 150 °K the signal is strongly chopped up, possibly as a result of the presence of nonequivalent protons in the system (two or more spin systems).

It is known that the times of the nuclear relaxation depend strongly on the concentration of the paramagnetic impurity. In this case, to explain the minimum of T_1 we have assumed dissociation of the Na atom and the presence of a localized electron as a paramagnetic center. A quantitative estimate of the minimum value $T_1 = 3.5\times 10^{-5}$ sec according to[3], $T_1 = 3d^3/4\pi N_s C$, where $d = (3\gamma_s/\gamma_1)^{1/4}a$, $C = 3\gamma_1^2\gamma_s^2\hbar^2/10\omega_0^2\tau_c$, $(\omega_0\tau_c > 1)$, $N_s = 6\times 10^{20}$ cm^{-3} is the Na concentration (2.5 at.%), $a = 1.65\times 10^{-8}$ cm is the distance between the protons in NH_3,[2] $\omega_0 = 2\pi f = 7.9\times 10^7$ sec^{-1}. γ_s and γ_1 are the gyromagnetic ratios of the electron and proton respectively), yields a correlation time $\tau_c = 1.5\times 10^{-7}$ sec. The reciprocal ESR line width in this system[4] ($\Delta H = 3$ G), $\tau = 1.2\times 10^{-7}$ sec, is close to this value. Moreover, calculation of the activation energy from the slope of the $\ln T_1(10^3/T)$ curve in the region 146—148 °K yields a value $E_a = 4.2$ eV, which is close to the sodium ionization potential 5.14 eV.

Thus, both the model with the conducting spiderweb of metallic sodium[1] and with the colloidal particles of metal[4] in solid ammonia do not contradict our results in the conducting temperature regions. It is difficult to see how, in the dielectric region, particles with dimension 0.2—0.5 μ, containing 10^8 Na atoms and so greatly decreasing the concentration of the possible paramagnetic centers can produce a more or less uniform distribution of the dissociated electrons in the volume. And furthermore the network of filaments of metallic sodium in the dielectric region breaks up upon dissociation of the sodium atom, thereby providing the nuclear system of the ammonia protons with a large concentration of paramagnetic centers on the one hand, and destroying the electric conductivity on the other.

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