

Hydration Effects in Chlorine³⁵ Nuclear Spin Resonance

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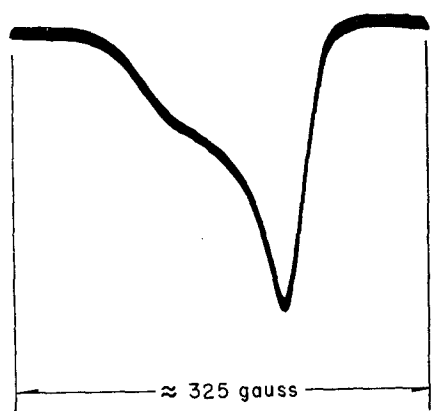


FIG. 1. The paramagnetic resonance absorption line observed at 23 000 Mc.

assayed. The ratio of molecules of H_2O_2 formed to unpaired electrons was found to be 154 in a sample prepared from water vapor. Somewhat similar ratios of 91 and 125 were found in material prepared from H_2O_2 and from hydrogen gas with subsequent addition of oxygen before condensing. Peroxide concentrations around 50% are found in the product made from H_2O . On this basis the samples contained roughly 0.3% by weight of radical if HO_2 is assumed or 0.15% for OH. Giguère⁴ has given infrared spectroscopic evidence for the presence of HO_2 in such materials. Foner and Hudson⁵ have analyzed with a mass spectrometer the OH, HO_2 , and H_2O_2 content in the gas phase from the reaction of H with O_2 . Their results indicate that if HO_2 is present in the frozen, glassy deposit, it was formed on the surface. On the basis of this evidence it would then appear that HO_2 is a likely radical giving rise to the absorption line in Fig. 1 and that the approximate 0.3% by weight content was built up from radical formation at the surface as the material condensed.

* This work was performed for the U. S. Atomic Energy Commission.

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² Livingston, Zeldes, and Taylor, *Phys. Rev.*, **94**, 725 (1954).

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Hydration Effects in Chlorine-35 Nuclear Spin Resonance*

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STRIKING evidence for the infrequent exchange of hydrate water with solvent in aqueous solutions of some paramagnetic ions results from observations on Cl^{35} nuclear spin resonance. The 0.2 gauss line width¹ between points of maximum slope for Cl^- in aqueous NaCl is apparently the uncertainty-principle width owing to the short lifetime of the nuclear spin states (short thermal relaxation time). If this assumption is correct, addition of paramagnetic ions to NaCl solutions should broaden the Cl^- line because of the relaxation induced by the large fluctuating magnetic fields of the ions. Starting with 3 M NaCl, the line amplitude is diminished and its width increased by Mn^{++} or Cu^{++} in concentrations of 2×10^{-4} M. Beyond a 6×10^{-3} M concentration of either ion the line is so broad that it escapes detection. The reagent-grade NaCl probably contained enough such impurities to give the observed line width. At 0.1 M concentrations of the ions Ti^{+++} , Cr^{+++} , Fe^{+++} , Co^{++} , and Ni^{++} in 3 M NaCl the relative signal amplitudes compared to the reference solution (3 M NaCl) are 0.1, 1.3, 0.07, 1.1, and 0.6, respectively. The order Mn^{++} , Cu^{++} , Fe^{+++} , Ti^{+++} , Ni^{++} , Co^{++} , and Cr^{+++} is that

of decreasing effectiveness in relaxation. Disregarding hydration, the order should be that of decreasing magnetic moment or (Fe^{+++} , Mn^{++}), Co^{++} , Cr^{+++} , Ni^{++} , Cu^{++} , and Ti^{+++} . For Co^{++} , Cr^{+++} , Nd^{+++} , and Sm^{+++} the relaxation effectiveness is low enough so that in dilute solutions of the pure salt the signal amplitude rises with concentration. Initial amplitude increases are found also in 3 M NaCl solutions dilute in Fe^{+++} , Ti^{+++} , Co^{++} , and Cr^{+++} . The line width for all ions studied increases from the lowest concentrations. The maximum amplitude for CoCl_2 occurs at 0.6 M, while it is at 1.4 M for CrCl_3 . The latter compound shows a Cl^- signal even at 3 M. At 1.4 M, the signal amplitudes for CrCl_3 and NdCl_3 are, respectively, 0.6 and 1.4 times those of 3 M NaCl. On adding Cr^{+++} to 3 M NaCl, the maximum amplitude appears at 0.4 M CrCl_3 . Thus, the maximum amplitude occurs at the same chloride ion concentration in the two cases.

The order of relaxation effectiveness is not the same as that for protons,^{2,3} but there it is probably the closeness of approach of the hydrate protons which is significant. Even for proton relaxation, Co^{++} shows an apparently low value of effective magnetic moment.² The paramagnetic anion $\text{Fe}(\text{CN})_6^{4-}$ at concentrations up to 1 M had no effect on Cl^- line amplitude, width, or position in 3 M NaCl, indicating a surprising lack of relaxation effectiveness.

The exchange of hydrate water in $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ for solvent has a half-period of 40 hours, while for Co^{++} and Fe^{+++} the reaction appears to be complete in less than two minutes.⁴ No corresponding rate information appears to be available for Ti^{+++} , Mn^{++} , Ni^{++} , and Cu^{++} . Mn^{++} and Cu^{++} probably exchange hydrate water with extreme rapidity and thus allow frequent close contacts with Cl^- ions. The activation energy for $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ water exchange has been given as 10 kcal per mole.⁵ The order of increasing activation energies should be ascertained for comparison with the relaxation-effectiveness series.

The line in NaCl was shifted to weaker fields by Cr^{+++} , Co^{++} , Ni^{++} , and Cu^{++} , while for Sm^{+++} the reverse was true. Ti^{+++} , Mn^{++} , Fe^{+++} , and Nd^{+++} showed no shift.

A detailed account of chloride and perchlorate ion resonance will be published.

Thanks are due Frisic Dravnieks who operated the spectrometer and to my colleagues R. Lumry, W. Reynolds, and Z. Z. Hugus for helpful discussions. The research was made possible by grants-in-aid from the Graduate School of the University.

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Abundance of Free Atoms in Solid Nitrogen Condensed at 4.2°K from a Gas Discharge*

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E1 This evidence consists mainly of a glow observed during the operation of the discharge and an afterglow persisting for several minutes, followed by a blue afterglow which appears at some higher temperature during the warming of the apparatus. The present experiments show that the latter afterglow probably occurs between 28°K and 35°K. Partial interpretation of the spectra of these glows has been proposed by Herzfeld and Broida in terms of the interaction of nitrogen atoms and molecules with the solid.²

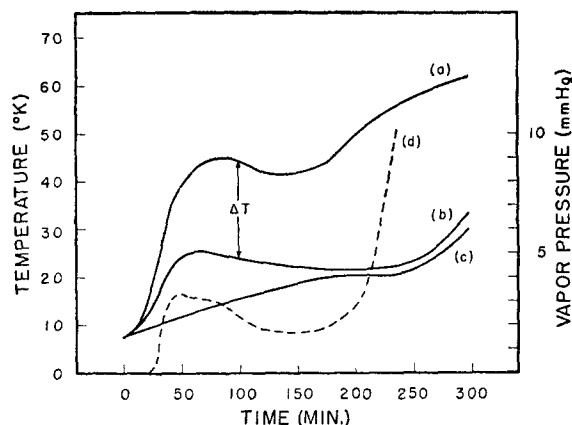


FIG. 1. (a) Condensed discharge products; (b) condensed molecular nitrogen; (c) glass collection chamber; and (d) measured vapor pressure of condensed discharge products.

In order to observe the thermal behavior associated with the visual and spectroscopic phenomena, we have measured the rate of temperature rise of the glass collection chamber after depositing material from the discharge. A large and rapid temperature change is observed in the warmup curve, and is attributed to the heat liberated by recombination of nitrogen atoms. Measurement of the temperature change and knowledge of the heat capacities of glass and solid nitrogen lead to an estimate of the heat liberated and the number of free atoms.

Two gold-cobalt vs silver-gold thermocouples³ were attached to the outside of the collection chamber,¹ one at the bottom and the other 3.5 cm higher. Absolute temperatures were determined with an accuracy of about one degree.[†]

Figure 1 shows warmup curves for (a) condensed discharge products, (b) molecular nitrogen condensed without discharge, and (c) for the blank chamber. Temperatures plotted are the average of the two thermocouple readings. Since the quantity of condensed nitrogen was the same, 0.18 mole, with and without discharge, it is reasonable to assume the observed temperature change for the discharge products is caused by recombination of nitrogen atoms. The observed rapid temperature rise for the molecular nitrogen without the discharge is thought to be due to the condensation of a small amount of nitrogen evaporated from warmer parts of the apparatus. Nevertheless, whatever the cause, this heating effect is less than $\frac{1}{3}$ that observed in the "atom" case.

An estimate of the abundance of nitrogen atoms in the solid can be obtained from the measured temperature change, ΔT , associated with the recombination. ΔT was taken as the vertical difference between the curves (a) and (b), at a time shortly after termination of the steep temperature rise, i.e., $\Delta T \approx 20^\circ\text{K}$. Using average values for specific heats over the temperature interval of the warmup, it is found that the total heat absorbed is about 47 calories—8 and 29 calories for heating the glass collection chamber and the solid nitrogen, respectively, and 10 calories for the phase change in molecular nitrogen at 35.6°K .⁴ Assuming the heat of dissociation of nitrogen to be 225 kilocalories per mole,⁵ a value of 0.2% is found for the concentration of atoms in the solid. Three separate sets of experiments gave results within a factor of 2 of the same value.

A separate experiment in which products were collected from a discharge through oxygen showed a concentration of 1% oxygen atoms in the solid.

* This work was supported by the Office of Naval Research.

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[†] We are indebted to M. Waxman, National Bureau of Standards, for furnishing the characteristics of the thermocouples for the temperature range 14–77°K.

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Specific Heat and Heat of Transformation of MgCd_3

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(Received August 2, 1955)

It is generally accepted that at room temperature the alloy Mg-Cd^1 has an ordered structure at the stoichiometric composition MgCd_3 . However, two investigations^{2,3} of this alloy in the vicinity of MgCd_3 are in disagreement with regard to the existence of an ordered state on the Cd-poor side. By making measurements of the specific heat as a function of temperature Nagasaki and co-workers² found that first-order transformations occur for compositions of 71.6 and 73.5 atomic percent of cadmium with Curie temperatures of 100°C and 94°C , respectively. On the other hand, Homiakov and co-workers³ made similar measurements on an alloy with 72.41 atomic percent of cadmium, and they found no evidence of any transformation between 35° and 158°C . The results of these investigations are shown in Table I.

It therefore seemed desirable to determine the specific heat curve for a Cd-poor alloy with composition near MgCd_3 . For this purpose a casting of such an alloy was prepared⁴ from cadmium and magnesium, 99.95 and 99.99% pure, respectively, by the method of Satterthwaite.⁵ This casting was subsequently homogenized in a helium atmosphere for 72 hours at 200°C , machined down to final size, and then kept at 80°C for 8 hours to permit it

TABLE I. Curie temperature T_c and total heat of transformation ΔH for compositions of the Mg-Cd alloy near MgCd_3 .

	Nagasaki <i>et al.</i> ^a			Homiakov <i>et al.</i> ^b			Present investigation
atom % Cd	71.6	73.5	76.5	72.41	75.15	72.14	
T_c in $^\circ\text{C}$	100	94	70	...	77	99.2	
ΔH in cal/g	>0	2.5	>0	0	2.6	2.53	
type transform	1st ord.	1st ord.	2nd ord.	...	2nd ord.	2nd ord.	

^a See reference 2.

^b See reference 3.

to come to equilibrium at this temperature. Chemical analyses were performed after the completion of the experiment on portions taken from each end and the middle of the cylindrical sample. The measurements agreed to within 0.02 atomic percent and the average content of Cd was 72.14 atomic percent.⁶

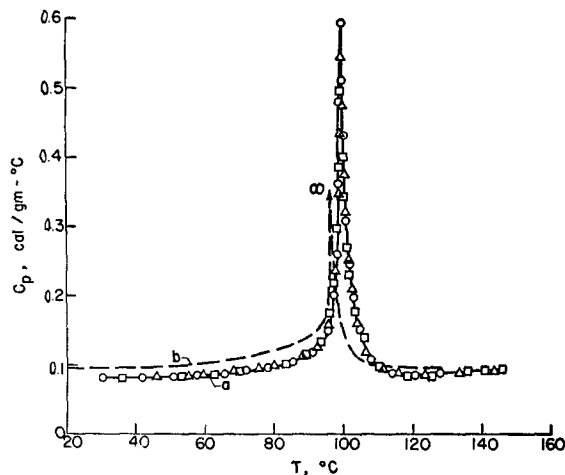


FIG. 1. Specific heat of Cd-poor MgCd_3 as a function of temperature. Curve a, 72.14 atomic percent Cd, present investigation; curve b, 73.5 atomic percent Cd, Nagasaki *et al.*²