

FIG. 1. Temperature dependence of the magnetic field required at fixed frequency for the  $\text{Na}^{23}$  nuclear resonance in the metal.  $\Delta H_r$  is the difference in applied fields; the field required for resonance in the metal is subtracted from  $H_a$ , the resonance field for  $\text{Na}^{23}$  in aqueous  $\text{NaCl}$ . The dashed line is a theoretical curve representing the effect of thermal expansion on paramagnetic susceptibility.

Fig. 1. The sample, from National Distillers Chemical Corporation, was a 25 percent sodium dispersion in Nujol mineral oil; particle sizes ranged from 1 to  $60\mu$ , averaging  $15\mu$ .  $\Delta H_r$  is the applied field,  $H_a$ , for resonance in aqueous  $\text{NaCl}$ , less that required for the metal. The resonance shift,  $\sigma \equiv 10^4 \times \Delta H_r / H_a$ , is relatively insensitive to temperature, varying by 5 percent from 210° to 425°K. Moreover, as suggested by Dr. C. P. Slichter in one of our discussions, most of the temperature dependence can be ascribed to volume effects. The alkali metals show a small increase with temperature in paramagnetic susceptibility, which Stoner attributes<sup>5</sup> to thermal expansion, on the basis of a free electron model. By analogy, the resonance shift would be  $\sigma_T = (V_T/V_0)^{1/3} \sigma_0$ , where the subscripts  $T$  and  $0$  refer to the given and a reference temperature, respectively, and  $V$  is the atomic volume. The dashed line in Fig. 1 represents this function, the reference temperature being chosen to be 25°C. The value of  $\sigma_0$  is taken to be 9.9, the experimental relative value of  $\sigma$  at 25°C. It is seen that the values computed at higher temperatures with the equation  $\sigma_T = (V_T/V_0)^{1/3} \times 9.9$  are lower than the observed  $\sigma$  by an amount that is proportional to the temperature effect on  $\sigma$ . This indicates that  $\sigma = 9.9$  measured with respect to the  $\text{NaCl}$  solution is not the absolute  $\sigma$  value. The experimental values should all be increased by 2, and the theoretical equation changed to  $\sigma_T = (V_T/V_0)^{1/3} \times 11.9$ , to put everything on an absolute scale and get the two curves to agree. The hysteresis in the resonance shift below the melting point probably results from super-cooling. The low temperature increase starting at 250°K appears to be real; similar results have been obtained for  $\text{Li}^7$ .

The temperature dependence of the  $\text{Na}^{23}$  resonance line width in the metal is given in Fig. 2. The transition at 190°K is presumably

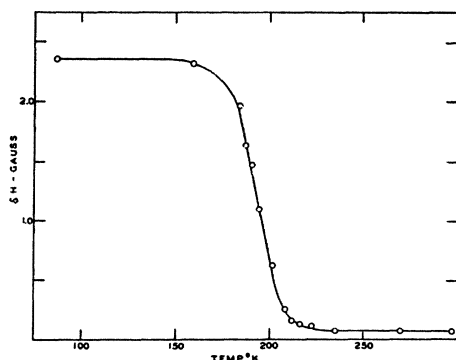


FIG. 2. The  $\text{Na}^{23}$  nuclear magnetic resonance line-width transition in the metal. The transition is consistent with an activation energy for self-diffusion of  $9.5 \pm 1.5$  kcal/g-atom. The measure of line-width used here is the peak-to-peak separation of the derivative of the absorption line.

associated with self-diffusion. An activation energy for self-diffusion of  $9.5 \pm 1.5$  kcal/g-atom is estimated<sup>6</sup> from the temperature and slope of the transition. The high temperature apparent line width of about 0.05 gauss is determined by field inhomogeneities and modulation effects. An independent analysis of the diffusion process is provided by the relaxation time measurements of Norberg and Slichter, which are presented and discussed in the accompanying letter.<sup>7</sup>

A comparison of Figs. 1 and 2 suggests that the low temperature increase in the resonance shift is perhaps associated with the diffusion process. For  $\text{Na}^{23}$  the increase in resonance shift starts at 255°K, a temperature about 65° above the line-width transition; in the case of  $\text{Li}^7$  the increase starts at a temperature about 85° above the line-width transition at 255°K. The time average magnetic resonance field at the nuclei could change as the diffusion rate becomes less than the Larmor frequency. In fact, the relaxation time data<sup>7</sup> and also the line-width observations for  $\text{Na}^{23}$  indicate the diffusion frequency is about 1 Mc at 250°K.

Various room temperature observations have been made. The  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$  resonance shifts in the metal with respect to  $\text{Cu}_2\text{Br}_2(s)$  were observed to be<sup>1</sup>  $23.46 \times 10^{-4}$ , within experimental error of  $\pm 0.5$  percent. Also, a chemical shift<sup>4</sup> of  $0.56 \times 10^{-4}$  was found between  $\text{Cu}_2\text{Cl}_2(s)$  and  $\text{Cu}_2\text{Br}_2(s)$  for  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$  with an experimental error of  $\pm 5$  percent;  $\text{Cu}_2\text{Br}_2(s)$  required the higher applied magnetic field. The  $\text{Al}^{27}$  resonance in  $\text{Al}^{+3}$  aqueous solution and in anhydrous  $\text{AlCl}_3(s)$  occurred in applied fields 0.81 and  $1.32 \times 10^{-4}$  higher than in  $\text{AlO}_2^-$  solution. Such chemical effects are an additional problem in the theoretical analysis<sup>2</sup> of resonance shifts in metals. The 20 percent factor suggested above for  $\text{Na}^{23}$  may reflect chemical effects; also, the temperature dependence itself complicates the issue.

Sodium, aluminum, and copper crystallize in cubic lattices for which electric quadrupolar broadening of the resonance line should be absent.<sup>8</sup> However, detailed line shape plots for the  $\text{Na}^{23}$  dispersion at 85°K and for  $\text{Al}^{27}$ ,  $\text{Cu}^{63}$ , and  $\text{Cu}^{65}$  in the powdered metals at room temperature gave experimental second moments of about 0.95, 11.7, 7.2, and 5.8 gauss<sup>2</sup> compared with theoretical second moments on the basis of magnetic dipolar broadening alone<sup>3</sup> of 0.66, 7.5, 5.1, and 3.4 gauss<sup>2</sup>, respectively. The high experimental values may result from anisotropy in the conduction electron shift in resonance frequency. Also, such anisotropy might generate electrical field gradients at the nuclei and lead to quadrupolar broadening. Experiments designed to determine the relative importance of the two factors include observation of metals with nuclear spin of  $\frac{1}{2}$ , the investigation of the dependence of second moments on applied field, and single-crystal studies.

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## Nuclear Relaxation Times in Metallic $\text{Na}^{23}$

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NUCLEAR magnetic relaxation times  $T_1$  (spin-lattice) and  $T_2'$  (spin phase-memory) have been measured in metallic sodium as a function of temperature from  $-58^\circ\text{C}$  to  $+80^\circ\text{C}$  using the spin-echo method.<sup>1</sup> The apparatus was a modified version of

that used by one of the authors to investigate hydrogen-palladium systems.<sup>2</sup> The sample was a dispersion of sodium in mineral oil as described in the accompanying letter.<sup>3</sup>

Within experimental error,  $T_1$  appears to be inversely proportional to the absolute temperature, in agreement with the theory of Heitler and Teller<sup>4</sup> regarding nuclear relaxation by interaction with the conduction electrons. From Korringa's theory<sup>5</sup> and Knight's measurement<sup>6</sup> of the frequency shift between  $\text{Na}^{23}$  resonances in the metal and in a salt, one calculates that  $T_1$  due to conduction electrons should equal 11.7 milliseconds at room temperature, in excellent agreement with the measured value of 9.2 milliseconds. A 20 percent increase in the shift, such as Gutowsky proposes in the accompanying letter,<sup>3</sup> would lower the theoretical  $T_1$  to a value even closer to the experimental result.

The  $T_2'$  data are shown in Fig. 1. Over the entire temperature range covered,  $T_2'$  is temperature dependent and is larger than the rigid lattice value by an order of magnitude. These results are in agreement with those of Gutowsky<sup>3</sup> which indicate that the line-width is narrower than the rigid lattice value for all temperatures above  $-100^\circ\text{C}$ . The spin echo results show that  $T_2'$  increases markedly with temperature from the lowest temperature at which spin echoes were observed ( $-58^\circ\text{C}$ ) to about  $-25^\circ\text{C}$ , where  $T_2'$  becomes of the order of  $T_1$ . For higher temperatures,  $T_2'$  goes as  $1/T$  within experimental error and is of the order of  $T_1$ , indicating that spin-lattice relaxation determines the line-width in the high temperature range.

Using a simple theory, the observed low temperature behavior of  $T_2'$  can be explained as the combined effect of spin-lattice line broadening and nuclear dipolar broadening.  $T_2'$  is assumed to be given by the equation

$$1/T_2' = (1/T_2) + 1/T_2^a, \quad (1)$$

where  $T_2$  is the phase-memory time determined by dipolar interactions alone, and  $T_2^a$  is that determined by spin-lattice interactions alone. The expression provides a better fit to the data than does the addition of second moments.

The large values observed for  $T_2'$  indicate that there is a motion of the sodium nuclei. Taking the motion to be self-diffusion of the nuclei, one may calculate the line narrowing on the basis of the theory of Bloembergen, Purcell, and Pound.<sup>7</sup> The calculation assumes the metal to be a liquid in which the atoms come no closer than a distance  $r$ , and predicts an exponential temperature dependence of  $T_2$  according to the law

$$\frac{1}{T_2} = \frac{4}{5} \frac{\gamma^4 \hbar^2 I(I+1) N e^{E/RT}}{r D_0}, \quad (2)$$

where  $\gamma$  is the nuclear gyromagnetic ratio,  $I$  is the nuclear spin,  $N$  the number of atoms per unit volume, and the diffusion constant,  $D$ , has been written in the customary form  $D = D_0 e^{-E/RT}$ . For numerical work  $r$  was taken to be the rigid-lattice nearest-neighbor distance  $3.7\text{\AA}$ . The liquid theory should give the temperature dependence of  $T_2$  rather well, but be less reliable in giving the actual magnitude of  $T_2$ .

To compare Eqs. (1) and (2) with experiment,  $T_2^a$  was taken to be a constant (10.8 milliseconds), since  $T_2^a$  is a much more slowly varying function of temperature than  $T_2$ . The work of Nachtrieb<sup>8</sup> has been utilized in the comparison. He has measured the coefficient of self-diffusion for sodium by means of radioactive tracers and finds  $D = 0.320 e^{-10650/RT}$   $\text{cm}^2/\text{sec}$ . Extrapolating his measurements to  $-56^\circ\text{C}$  gives  $D = 0.74 \times 10^{-11}$   $\text{cm}^2/\text{sec}$ . The nuclear resonance data at this temperature, where the  $T_2^a$  correction is small, yield  $D = 1.3 \times 10^{-11}$   $\text{cm}^2/\text{sec}$ . The order of magnitude agreement is considered satisfactory, since the theory is somewhat crude.

To compare the temperature dependence of the nuclear resonance data with Nachtrieb's results, a theoretical  $T_2'$  curve was constructed. Equations (1) and (2) and the constant  $T_2^a$  were used to calculate a value of  $T_2$  at  $-56^\circ\text{C}$  from the data. This value of  $T_2$ , together with  $T_2^a$  and Nachtrieb's value of the activation energy, determined the theoretical  $T_2'$  curve shown in Fig. 1. Curves corresponding to values of activation energy 20 percent

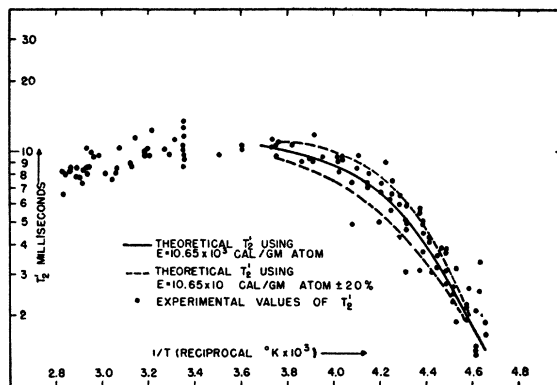


FIG. 1. Temperature dependence of  $T_2'$  for metallic  $\text{Na}^{23}$ .

higher and lower are also shown. The agreement of both the temperature dependence and the order of magnitude of  $D$  with Nachtrieb's results confirms the hypothesis of diffusion narrowing. Similar work is currently in progress on the  $\text{Li}^7$  relaxation times.

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## Nuclear Absorption of Negative Pi-Mesons at Different Energies

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ILFORD G-5, 400-, and 600-micron nuclear emulsions were exposed to the 70- and 105-Mev external  $\pi^-$  meson beams of the Nevis cyclotron, and the analysis of the interaction with emulsion nuclei was continued.<sup>1,2</sup> To extend the energy range, additional plates were exposed to the 70-Mev beam behind 8'' of lithium plus  $\frac{1}{2}$ '' of carbon. The energy of the mesons crossing these plates was 30-50 Mev, as determined by plural scattering and grain density

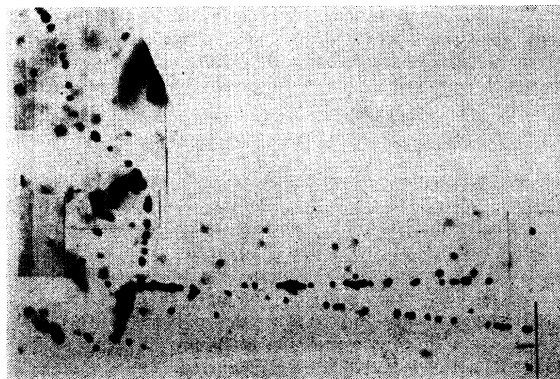


FIG. 1. Backward elastic scattering ( $E = 105$  Mev,  $\Theta = 173^\circ$ ) with recoil and slow electron at the vertex (observed by Mrs. N. Bernardini).