where K is the low frequency dielectric constant, K_0 is the optical constant, ρ the density, and χ the compressibility. In Table I are listed the values of $\partial \ln K/\partial p$ calculated from (4) and (1) next to the experimental values of $\partial \ln K/\partial p$. The calculated values of $\partial \ln K/\partial p$ differ from those of Rao by the term $a(K-K_0)/K$, which arises from the difference between (1a) and (2a).

Equation (4) is derived assuming that the inner field polarizing the dielectric is independent of pressure. Since the values of $-\partial \ln K/\partial p$ obtained from (4) do not account for all the change in the dielectric constant, it seems consistent to expect that the inner field is not constant but does decrease with increasing pressure. This conclusion agrees with the one reached in my original paper using the theories of Hojendahl and Mott and Littleton.

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Radiative Transition Probabilities in Nuclei

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CONSIDER a transition from nuclear state a to nuclear state b with emission of a quantum of multipole radiation of angular momentum l (2^l-pole) and z component m. The transition probability per unit time is given by[1]

$$T(l, m) = \frac{8\pi(l+1)}{l[(2l+1)!!]^2} \frac{\kappa^{2l+1}}{\hbar} |A(l, m) + A'(l, m)|^2, \qquad (1)$$

where $\kappa = 2\pi\nu/c$ is the wave number of the emitted radiation, and the quantities A, A' are the multipole matrix elements caused by the electric currents and by the magnetization (spins), respectively. We find for electric radiation

$$A(l, m) = Q(l, m) = e \sum_{k=1}^{z} \int r_k{}^l \, Y_{lm}{}^*(\theta_k, \phi_k) \, \varphi_b{}^* \varphi_a \, d\tau, \qquad (2)$$

$$A'(l, m) = Q'(l, m) = -\frac{i\kappa}{l+1} \frac{e\hbar}{2Mc} \sum_{k=1}^{A} \mu_k$$

$$\times \int r_k{}^l \, Y_{lm}{}^*(\theta_k, \phi_k) \, \mathrm{div}(\varphi_b{}^* \mathbf{r}_k \times \boldsymbol{\sigma}_k \varphi_a) \, d\tau, \qquad (3)$$

where φ_a and φ_b are the wave functions of the nuclear states, M is the mass of each nucleon, $\mathbf{r}_k = (r_k, \theta_k, \phi_k)$ is the position vector of the kth nucleon, $\boldsymbol{\sigma}_k$ is its Pauli spin vector, and μ_k is its magnetic moment in nuclear magnetons. The sum in (2) extends over the protons, the sum in (3) over both protons and neutrons. These expressions are approximations valid for $\kappa R \ll 1$, where R is the nuclear radius.

The corresponding expressions for magnetic multipole radiation are

$$A(l, m) = M(l, m) = -\frac{1}{l+1} \frac{e\hbar}{Mc} \sum_{k=1}^{z}$$

$$\times \int r_k{}^l \, Y_{lm}{}^*(\theta_k, \phi_k) \, \mathrm{div}(\varphi_b{}^* \mathbf{L}_k \varphi_a) \, d\tau, \qquad (4)$$

$$A'(l, m) = M'(l, m) = -\frac{e\hbar}{2Mc} \sum_{k=1}^{A} \mu_k$$

$$\times \int r_k{}^l \, Y_{lm}{}^*(\theta_k, \phi_k) \, \mathrm{div}(\varphi_b{}^* \boldsymbol{\sigma}_k \varphi_a) \, d\tau, \qquad (5)$$

where $\mathbf{L}_k = -i\mathbf{r}_k \times \nabla_k$ is the orbital angular momentum operator (in units of $\hbar$) for the kth nucleon.

We can estimate these matrix elements by the following exceedingly crude method. We assume that the radiation is caused by a transition of one single proton which moves independently within the nucleus, its wave function being given by $u(r) Y_{lm}(\theta, \phi)$. In addition we also assume that the final state of the proton is an S state.[2] We then obtain

$$Q(l, m) \sim [e/(4\pi)^{\frac{1}{2}}][3/(l+3)] R^l \qquad (6)$$

where the integral $\int r^l u_b(r) u_a(r) r^2 dr$ over the radial parts of the proton wave functions was set approximately equal to $3R^l/(l+3)$. The other matrix elements are estimated by replacing div by R^{-1}. We get the rough order-of-magnitude guess

$$M(l, m) \sim [e/(4\pi)^{\frac{1}{2}}][3/(l+3)][\hbar/Mc] R^{l-1}, \qquad (7)$$

$$M'(l, m) \sim [e/(4\pi)^{\frac{1}{2}}][3/(l+3)] \mu_P [\hbar/Mc] R^{l-1}, \qquad (8)$$

where μ_P is the magnetic moment of the proton ($=2.78$). $Q'(l, m)$ can be neglected compared to $Q(l, m)$. We therefore get a ratio of roughly

$$(1+\mu_P{}^2)(\hbar/McR)^2 \sim 10(\hbar/McR)^2$$

between the transition probability of a magnetic multipole and an electric one of the same order. This ratio is energy-independent in contrast to widespread belief.

Inserting these estimates into (1) we get for the transition probability of an electric 2^l-pole

$$T_E(l) \cong \frac{4.4(l+1)}{l[(2l+1)!!]^2} \left(\frac{3}{l+3}\right)^2 \left(\frac{\hbar\omega}{197 \text{ Mev}}\right)^{2l+1}$$

$$\times (R \text{ in } 10^{-13} \text{ cm})^{2l} \, 10^{21} \text{ sec}^{-1} \quad (9)$$

and for a magnetic 2^l-pole

$$T_M(l) \cong \frac{1.9(l+1)}{l[(2l+1)!!]^2} \left(\frac{3}{l+3}\right)^2 \left(\frac{\hbar\omega}{197 \text{ Mev}}\right)^{2l+1}$$

$$\times (R \text{ in } 10^{-13} \text{ cm})^{2l-2} \, 10^{21} \text{ sec}^{-1}. \quad (10)$$

The assumptions made in deriving these estimates are extremely crude and they should be applied to actual transitions with the greatest reservations. They are based upon an extreme application of the independent-particle model of the nucleus and it was assumed that a proton is responsible for the transition. On the basis of our assumptions the electric multipole radiation with $l>1$ should be much weaker for transitions in which a single neutron changes its quantum state. No such differentiation is apparent in the data.

In spite of these difficulties it may be possible that the order of magnitude of the actual transition probabilities is correctly described by these formulas. We have published these exceedingly crude estimates only because of the rather unexpected agreement with the experimental material which was pointed out to us by many workers in this field.

[1] We use the notation $(2l+1)!! = 1 \cdot 3 \cdot 5 \cdots (2l+1)$.
[2] This latter assumption can be removed; the corrections consist in unimportant numerical factors.

Nuclear Magnetic Resonance in Metals: Temperature Effects for Na²³

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KNIGHT reported[1] that nuclear magnetic resonance frequencies are higher in metals than in chemical compounds. It has been proposed[2] that such frequency shifts are primarily the result of the contribution of conduction electrons to the magnetic field at the nuclei in the metal. This note gives an account of some related preliminary results including temperature and chemical effects, and also detailed line shape studies. Our experiments have been at fixed frequency using equipment and procedures outlined previously.[3, 4]

The effect of temperature on the Na²³ magnetic resonance shift in the metal, relative to a sodium chloride solution, is given in
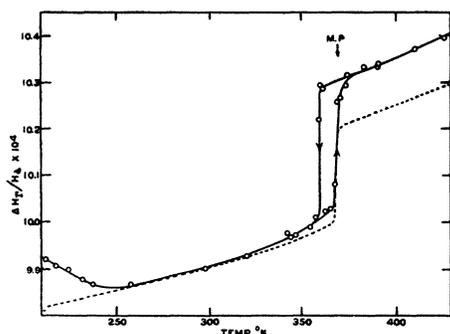
FIG. 1. Temperature dependence of the magnetic field required at fixed frequency for the Na²³ nuclear resonance in the metal. ΔH_r is the difference in applied fields; the field required for resonance in the metal is subtracted from H_a, the resonance field for Na²³ in aqueous NaCl. The dashed line is 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 60μ, averaging 15μ. ΔH_r is the applied field, H_a, for resonance in aqueous NaCl, less that required for the metal. The resonance shift, $\sigma = 10^4 \times \Delta H_r/H_a$, 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[5] to thermal expansion, on the basis of a free electron model. By analogy, the resonance shift would be $\sigma_T = (V_T/V_0)^{\frac{1}{3}}\sigma_0$, 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 σ_0 is taken to be 9.9, the experimental relative value of σ at 25°C. It is seen that the values computed at higher temperatures with the equation $\sigma_T = (V_T/V_0)^{\frac{1}{3}} \times 9.9$ are lower than the observed σ by an amount that is proportional to the temperature effect on σ. This indicates that $\sigma = 9.9$ measured with respect to the NaCl solution is not the absolute σ value. The experimental values should all be increased by 2, and the theoretical equation changed to $\sigma_T = (V_T/V_0)^{\frac{1}{3}} \times 11.9$, 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 Li⁷.

The temperature dependence of the Na²³ resonance line width in the metal is given in Fig. 2. The transition at 190°K is presumably
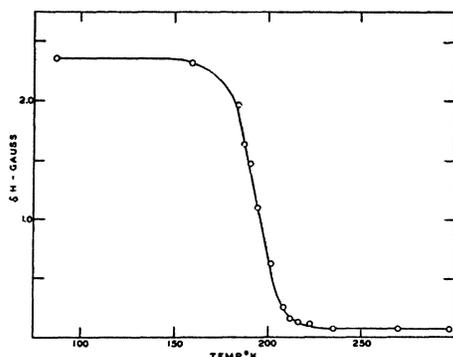
FIG. 2. The Na²³ nuclear magnetic resonance line-width transition in the metal. The transition is consistent with an activation energy for self-diffusion of 9.5±1.5 kcal/g-atom. The measure of line-width used here is the peak-to-peak separation of the derivative of the absorption line.

associated with self-diffusion. An activation energy for self-diffusion of 9.5±1.5 kcal/g-atom is estimated[6] 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.[7]

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 Na²³ the increase in resonance shift starts at 255°K, a temperature about 65° above the line-width transition; in the case of Li⁷ 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[7] and also the line-width observations for Na²³ indicate the diffusion frequency is about 1 Mc at 250°K.

Various room temperature observations have been made. The Cu⁶³ and Cu⁶⁵ resonance shifts in the metal with respect to Cu₂Br₂(s) were observed to be[1] 23.46×10⁻⁴, within experimental error of ±0.5 percent. Also, a chemical shift[4] of 0.56×10⁻⁴ was found between Cu₂Cl₂(s) and Cu₂Br₂(s) for Cu⁶³ and Cu⁶⁵ with an experimental error of ±5 percent; Cu₂Br₂(s) required the higher applied magnetic field. The Al²⁷ resonance in Al⁺³ aqueous solution and in anhydrous AlCl₃(s) occurred in applied fields 0.81 and 1.32×10⁻⁴ higher than in AlO₂⁻ solution. Such chemical effects are an additional problem in the theoretical analysis[2] of resonance shifts in metals. The 20 percent factor suggested above for Na²³ 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.[8] However, detailed line shape plots for the Na²³ dispersion at 85°K and for Al²⁷, Cu⁶³, and Cu⁶⁵ in the powdered metals at room temperature gave experimental second moments of about 0.95, 11.7, 7.2, and 5.8 gauss² compared with theoretical second moments on the basis of magnetic dipolar broadening alone[3] of 0.66, 7.5, 5.1, and 3.4 gauss², 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 Na²³

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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°C to +80°C using the spin-echo method.[1] The apparatus was a modified version of