for enlightening discussions, and W. F. Brinkman for his continued interest in this project. One of us (M.L.) acknowledges a Fellowship from the Schweizerischer Nationalfonds.

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Critical Nuclear Magnetic Relaxation in a Strong Itinerant-Electron Ferromagnet: Ni

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Nuclear magnetic resonance has been observed in ferromagnetic Ni near the critical temperature. The nuclear spin-spin and spin-lattice relaxation rates are found to become equal in the critical region below T_C and diverge with a critical exponent $n' = 0.67 \pm 0.08$. Spin-lattice relaxation rates in the paramagnetic state exhibit only incipient spin-fluctuation enhancement within the experimental range. Measurements of the ferromagnetic NMR frequency near T_C and of the Knight shift above T_C are described.

The three-dimensional (3D) transition metals Fe, Co, and Ni are among the most familiar magnetic materials, yet experimental data on critical spin-fluctuation phenomena in these systems are few and contradictory. Ni has the lowest Curie temperature of the three ($T_C = 631$ K) and fluctuations in Ni have been investigated by inelastic neutron scattering[1] and by the method of time-differential perturbed angular correlations (PAC) in the paramagnetic state.[2] However, the temperature dependences of the spin correlation times obtained in these experiments differ from each other and from the prediction of dynamic scaling theory.[3] Nuclear magnetic relaxation measurements also probe spin-fluctuation phenomena and have been applied to the study of insulating[4,5] and weak itinerant-electron[6-9] magnetic systems. However, experimental difficulties have until now prohibited NMR studies in the vicinity of the critical temperature for any of the 3D metals. We have found that these problems can be overcome by taking sufficient care in reducing temperature inhomogeneities, and we have measured the resonant frequency and nuclear relaxation rates, $1/T_1$ and $1/T_2$, in the ferromagnetic state of Ni to values of the reduced temperature $\epsilon_- \equiv 1 - T/T_C \simeq 2\times 10^{-3}$. These improvements in technique have also permitted measurements above T_C which significantly extend previous NMR work[10] on paramagnetic Ni although a minimum value of only $\epsilon_+ \equiv T/T_C - 1 \simeq 0.15$ could be achieved.

The most serious difficulty in performing NMR measurements near the critical point in either the ferromagnetic or the paramagnetic state is the presence of severe inhomogeneous broadening. This arises from the combined effects of sample temperature inhomogeneities and strongly temperature-dependent NMR frequencies. In the present work high thermal homogeneity was achieved by observing the NMR of nuclei within the skin depth of a single toroidal piece of Ni rather than by using the more usual powder sample. In addition special care was taken to optimize the temperature homogeneity within the furnace. Because of larger rf heating effects, these measures were less successful above T_C than below.

The sample[11] was prepared from enriched ^{61}Ni (92.9%) to overcome the low natural abundance of this isotope and measurements were made using pulsed NMR techniques. In the ferromagnetic state, frequencies $(\omega_0/2\pi)$ in the range 4–26 MHz were observed with no applied magnetic field. Since high rf fields were employed, these signals arose mainly from nuclei at the edge of the domain walls having properties essentially representative of the bulk.[12] In the paramagnetic state, a fixed frequency of 17 MHz was employed with applied fields in the range 44–50 kG.

Data relating to the static magnetization are summarized and compared with previous results[10,13] in Fig. 1. For $T<T_C$, the NMR frequency $\nu(T)$ approaches zero at T_C and since $\nu(T)$ is proportional to the magnetization $M(T)$ we can write $\nu \propto M \propto \epsilon_-^{\,\beta}$. A least-squares fit to a power law over the range $2\times10^{-3} \lesssim \epsilon_- \lesssim 1\times10^{-1}$ yielded $\beta = 0.354 \pm 0.014$ and $T_C = 632.7 \pm 0.4$ K with the error limits corresponding to twice the standard error of the fit. Our value of the exponent β is in agreement with the value 0.358 ± 0.003 recently obtained by Cohen and Carver from microwave transmission studies[14] while differing from the

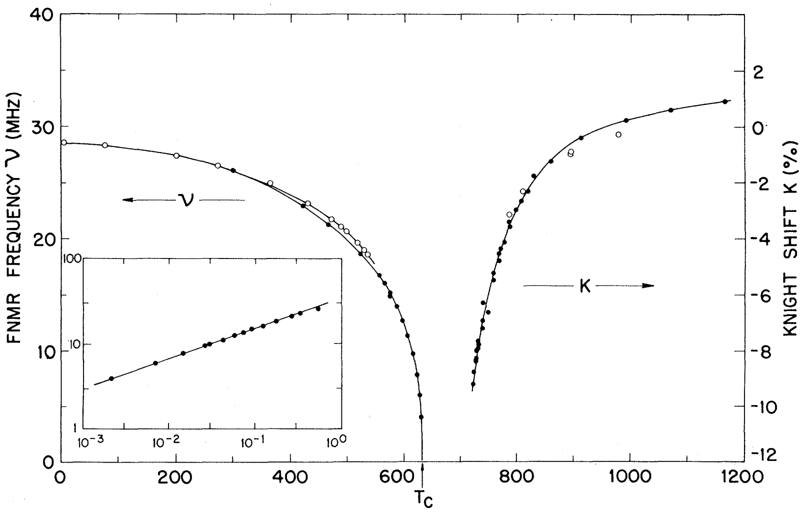

FIG. 1. Zero-field NMR frequency $\nu(T)$ (left-hand scale) and Knight shift $K(T)$ (right-hand scale) for ferromagnetic and paramagnetic Ni, respectively (closed circles). Also shown (open circles) are lower-temperature $\nu(T)$ data of Streever and Bennett (Ref. 13) and $K(T)$ data of Segransan *et al.* (Ref. 10). Inset: Log-log plot of $\nu(T)$ vs $\epsilon_- \equiv 1 - T/T_C$. The solid line corresponds to $\beta = 0.354$.

value 0.385 ± 0.005 found by Reno and Hohenemser[15] using PAC in dilute *Ni*:Rh.

The Knight shift in the paramagnetic state (Fig. 1) was measured relative to a reference magnetic field given by the nuclear gyromagnetic ratio $\gamma_{61} = 0.379$ kHz/G.[16] On approaching T_C, the shift diverges in the *negative* direction because of the dominant d-spin component of the magnetic field with its negative core-polarization hyperfine field. Qualitatively similar data have been reported previously for paramagnetic Co ($\epsilon_+ \geqslant 0.11$)[17] and Ni ($\epsilon_+ \geqslant 0.2$),[10] although there is a clear quantitative discrepancy between our data and those of Ref. 10 in the high-temperature range. We can offer no explanation for this but remark that the discrepancy cannot be due to the demagnetization factor correction which we estimate to be $\lesssim 2\%$ of the observed shift.

The **d**-spin hyperfine field $H_{\text{hf}}{}^d$ was obtained from a linear correlation of the Knight shift and magnetic susceptibility[18] according to the method of Clogston, Jaccarino, and Yafet.[19] Using a weighted least-squares fit we find $\Delta K/\Delta\chi_m = -24.5 \pm 1.2$ mole/emu or $H_{\text{hf}}{}^d = -137 \pm 7$ kG/μ_B. Assumption of a value[20] $H_{\text{hf}}{}^{\text{orb}} \simeq 560$ kG/μ_B yields a temperature-independent orbital susceptibility component $\chi_{\text{orb}} = 0.19 \pm 0.05 \times 10^{-3}$ emu/mole.

Critical dynamics determines the behavior near T_C of the nuclear spin-lattice relaxation rate ($1/\boldsymbol{T}_1$) and spin-spin relaxation rate ($1/T_2$). Experimental values for these rates are shown in Fig. 2 plotted in the form $(T_1T)^{-1}$ versus temperature. Far from T_C, it is evident that $(T_1T)^{-1}$ is essentially constant and nearly equal in the ferromagnetic and paramagnetic states. Well below T_C, values of $(T_2T)^{-1}$ are substantially larger than $(T_1T)^{-1}$, but we find that $(T_2T)^{-1}$ begins to decrease rapidly above about 500 K.[21] Both $(T_1T)^{-1}$ and $(T_2T)^{-1}$ exhibit divergent behavior as $\epsilon_- \to 0$ and a slight enhancement of $(T_1T)^{-1}$ is apparent at the lowest temperatures in the paramagnetic phase.

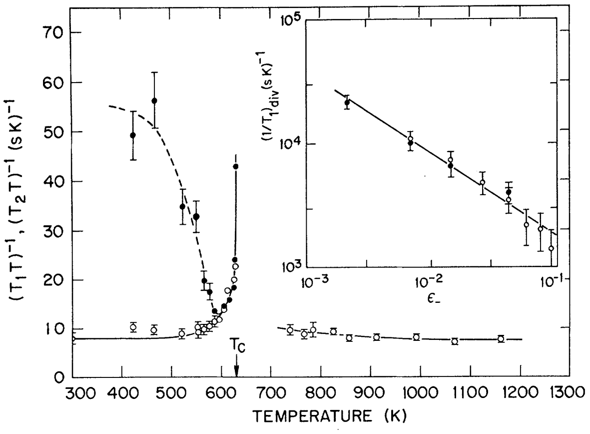

FIG. 2. Spin-lattice and spin-spin relaxation rates plotted, respectively, as $(T_1T)^{-1}$ (open circles) and $(T_2T)^{-1}$ (closed circles) vs temperature. Inset: Log-log plot of divergent portion of relaxation rate [second term of Eq. (1)] vs ϵ_- for ferromagnetic Ni. The solid line corresponds to $n' = 0.67$.

The nuclear relaxation rates in the critical region can be represented as the sum of a background contribution and a diverging term according to

$$(T_1)^{-1} = (T_2)^{-1} = (8.0 \pm 1.0)T + (380 \pm 40)\epsilon_-^{-n'}\ \text{s}^{-1}, \tag{1}$$

where the power-law exponent is $n' = 0.67 \pm 0.08$. The exponent agrees within experimental error with the value $n = 0.70 \pm 0.03$ measured above T_C by PAC.[2] The background relaxation is generally believed to result mainly from orbital interactions although complete agreement of theory and experiment is still lacking.[22-25]

The spin-lattice relaxation rate near T_C is governed by fluctuations of the transverse electron-spin components[26]

$$1/T_1 = 2(\gamma_n H_{\text{hf}}{}^d)^2 \int_{-\infty}^{\infty} dt \exp(-i\omega_0 t) G_{+-}(0; t), \tag{2}$$

where $G_{+-}(0; t)$ is the correlation function for fluctuations of the transverse spin operator, $G_{+-}(0; t) = \langle \delta S_+(r=0; t)\delta S_-(r=0; 0)\rangle$, and γ_n is the nuclear gyromagnetic ratio. In terms of the Fourier transform of $G_{+-}(\vec{r}; t)$ we have

$$1/T_1 = 2(\gamma_n H_{\text{hf}}{}^d)^2 \int d^3k\, G_{+-}(\vec{k}; \omega_0). \tag{3}$$

A similar expression applies for the spin-spin relaxation rate (linewidth) except that an additional term is present involving the longitudinal function $G_{zz}(\vec{k}; \omega_0)$:

$$1/T_2 = 1/2T_1 + (\gamma_n H_{\text{hf}}{}^d)^2 \int d^3k\, G_{zz}(\vec{k}; 0). \tag{4}$$

The transverse and longitudinal correlation functions are expected to have the same critical behavior so that $1/T_1$ and $1/T_2$ should yield the same critical exponent n'.[27] However, our observation that $1/T_1 \simeq 1/T_2$ in the critical region implies a stronger condition, namely

$$\int d^3k\, G_{+-}(\vec{k}; 0) \equiv \int d^3k\, [G_{xx}(\vec{k}; 0) + G_{yy}(\vec{k}; 0)] \cong \int d^3k\, G_{zz}(\vec{k}; 0). \tag{5}$$

This isotropy of the integrals is surprising since the correlation functions themselves are expected to become isotropic only in the limit $k \gg \kappa$ where κ is the inverse correlation length.[27]

The prediction of dynamic scaling theory for the divergence of Eqs. (3) and (4) has been discussed by Halperin and Hohenberg for an isotropic Heisenberg ferromagnet.[3] Their result can be written $n = n' \simeq 2\nu' - \beta$ where ν' is the exponent describing the divergence of the correlation length, i.e., $\kappa^{-1} \sim \epsilon_-^{-\nu'}$. Since $\nu' \simeq \frac{2}{3}$ (Ref. 3) and $\beta \simeq 0.36$, the dynamic scaling relation predicts $n = n' \simeq 0.97$. Thus the predicted exponent is in disagreement with both the NMR and PAC results. The question remains open, however, whether this represents a real failure of dynamic scaling theory or merely demonstrates the inapplicability of the Heisenberg model to an itinerant-electron ferromagnet such as Ni. It is possible, of course, that the NMR and PAC experiments have not been performed sufficiently close to T_C to have reached the asymptotic limit, although it seems unlikely that the full discrepancy could be explained in this way.

In summary, we have found that by minimizing thermal inhomogeneities it is possible to observe critical nuclear relaxation phenomena by NMR in ferromagnetic Ni. The critical exponent for the relaxation rate below T_C agrees within experimental error with that determined by PAC above T_C but both stand in disagreement with the prediction of dynamic scaling theory for the isotropic Heisenberg ferromagnet. Essentially no critical relaxation was observed in the paramagnetic state because of the difficulty of detecting the resonance close to T_C. The static properties are consistent with expectations for a $3d$ transition metal. However the relaxation studies demonstrate an obvious need for a more complete theory of spin dynamics in a strong, itinerant-electron ferromagnet.

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[a] This work forms part of a thesis to be submitted by M. Shaham to the Weizmann Institute of Science in partial fulfillment of the requirements for the PhD. degree.

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Inverse Isotope Effect and the x Dependence of the Superconducting Transition Temperature in PdH_x and PdD_x

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First-principles electronic–band-structure calculations and measured phonon properties are employed in a calculation of the concentration dependence of the superconducting transition temperatures for PdH_x and PdD_x, including the inverse isotope effect. Excellent agreement with the experimental results is obtained. Our model also gives a qualitative understanding of the enhanced transition temperatures in the palladium–noble-metal hydrides.

Since the discovery[1,2] of superconductivity in PdH_x and PdD_x with $x \gtrsim 0.8$, it has been well established that the role of the hydrogen or deuterium optic-mode vibrations is fundamental in determining the superconducting properties of these systems. Ganguly[3] has emphasized the importance of the H or D "local modes" in PdH_x (PdD_x) based on purely theoretical considerations, while Papaconstantopoulos and Klein,[4,5] and Switendick[6] have done detailed calculations of the superconducting transition temperatures, T_c, which have put these theoretical ideas on a firm quantitative basis. Recent tunneling measurements[7-9] have, at least qualitatively, verified the conclusions of these works.

In this Letter we have extended the work of Refs. 4 and 5 to examine in a quantitative way the question of the inverse isotope effect[10-13] and the x dependence of T_c[10-14] in PdH_x (PdD_x). Furthermore, our analysis provides a qualitative explanation for the occurrence of even higher values of T_c in the palladium–noble-metal hydrides.[15] We have employed *ab initio* augmented-plane-wave (APW) band-structure calculations, and measured phonon densities of states (DOS) to obtain T_c for PdH_x (PdD_x); no adjusted parameters are used. The agreement between theory and experiment is remarkable, and strongly indicates that a basic understanding of superconductivity in the palladium-hydrogen (-deuterium) system is at hand. Further experimental checks of our interpretation are suggested.

The inverse isotope effect is attributed to the effective increase of the Pd-H force constant, $k_{\text{Pd-H}}$, over $k_{\text{Pd-D}}$, due to enhanced anharmonicity of the H motion, as originally proposed by Ganguly. Rahman *et al.*[16] have found, by analyzing their neutron scattering measurements on $PdH_{0.63}$, and comparing them with the $PdD_{0.63}$ data,[17] that $k_{\text{Pd-H}} \approx 1.2 k_{\text{Pd-D}}$, which leads to a 20% increase in $\langle\omega^2\rangle_D M_D/M_H$. We show here that this increase is enough to account quantitatively for the observed inverse isotope effect.

The x dependence of T_c in PdH_x (PdD_x) is mainly due, according to the present analysis, to a rapid increase of the average electron–optic-phonon (i.e., H or D vibration) interaction, λ_{opt}, as x approaches 1. Although the total electronic DOS decreases as x increases, the H- or D-site components of the DOS (see Fig. 1) rise[6,18] in a way such that λ_{opt} increases with x. In effect, more electrons are found in the vicinity of the H or D sites with increasing H or D concentration. This effect continues for $x > 1.0$, and we argue that this is the explanation for the enhanced T_c's in the palladium–noble-metal hydrides.

Our detailed calculations of T_c are based on solutions to the linearized Eliashberg equations,[19] which have as input the quantities $\alpha^2(\omega)F(\omega)$ and μ^*. Here $F(\omega)$ is the phonon DOS; $\alpha^2(\omega)$ contains the pairing electron-phonon interaction; and μ^* is the pair-breaking Coulomb pseudopotential. We calculated T_c also using the McMillan-type[20] equation proposed by Allen and Dynes[21] with results which agree within 10% of the Eliashberg-equation solutions.

Making use of the theory of Gaspari and Gyorffy,[22] and a generalization to compounds[23,24] of