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Ti NMR Study of the Nearly Ferromagnetic System TiBe$_2$

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NMR data on TiBe$_2$ have been taken from 1.3 to 270 K in magnetic fields up to 60 kG. The linear dependence of the Knight shift and the NMR linewidth with $\chi = M/H$ show that the increase of χ versus applied field at low temperatures is due to a homogeneous property of the electron gas. The d-electron contribution to the spin-lattice relaxation rate is found to scale linearly with χT in a wide temperature range spanning the spin-fluctuation temperature.

The properties of the intermetallic compound TiBe$_2$ have attracted considerable interest in recent years. This cubic C-15 type material has a strongly enhanced, temperature-dependent susceptibility[1,2] and at low temperatures the $\chi = M/H$ susceptibility changes with the magnetic field[3,4] and shows a maximum at about 50 to 60 kG. The large enhancement of the susceptibility without any long-range magnetic ordering at low temperature, together with the specific heat, resistivity,[5,6] and ESR data[7] show that the electronic system in TiBe$_2$ exhibits the properties of an interacting Fermi liquid with a low spin-fluctuation temperature[8] ($T_{sf} \sim 20$ to 50 K). The consequences of the interactions on a microscopic scale, the behavior of the dynamic susceptibility, and the origin of the field-dependent χ are open problems which call for more experimental work. On the other hand, the influence of sample preparation on some macroscopic properties, such as the magnitude of the maximum of M/H, is apparent in the early publications.[3,4] More systematic investigations as a function of preparation techniques are presently attempted.[6] It is quite important to determine whether the differences in the macroscopic parameters are induced mainly by homogeneous modifications of the electronic structure, by sample inhomogeneities, or by local environment effects around impurities. NMR as a microscopic probe is well suited to clear up this point and to provide information on the dynamical susceptibility through nuclear relaxation measurements.

In this Letter we present NMR investigations on the Ti nuclei in a wide range of fields and temperatures. The TiBe$_2$ sample was prepared by Monod et al.[4] and before reduction into powder for the NMR measurements it has been heat treated in vacuum at 800 K for 100 h. The resistivity ratio $r = \rho(300 \text{ K})/\rho(4.2 \text{ K})$, the low-field susceptibility χ (10 kG), and the susceptibility ratio $p = \chi(60 \text{ kG})/\chi(10 \text{ kG})$ were $r = 36$, $\chi(10) = 8.4 \times 10^{-3}$ emu/mole, and $p = 1.18$, respectively, after annealing. On the other hand $r = 110$, $\chi(10) = 9.7 \times 10^{-3}$ emu/mole, and $p = 1.27$ were found on a sample prepared in Los Alamos, which confirms the different results of Refs. 3 and 4 and shows that our sample is adequate for investigating any problem linked with sample homogeneity.

The NMR spectra were taken with a phase-coherent spectrometer operating at a fixed frequency in the range from 5 to 16 MHz. The magnetic field was calibrated by measuring the NMR signal of ^{109}Ag in a silver sample[9] located in the same sample holder as the TiBe$_2$. We recorded the full integral of the spin echo versus magnetic field. The pulse separation time ($\tau \lesssim 400$ μsec) was always much shorter than the time decay of the spin echo.

At 272 and 77 K the Knight shifts were $K = (0.09 \pm 0.01)\%$ and $-(0.49 \pm 0.005)\%$ in good agreement with the results of Saji et al.[1] and slightly differing from the values estimated from the more recent measurements of Takayi et al.[10] At 1.3 K

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we found that the Knight shift increases with the magnetic field (Fig. 1, inset) as does $\chi = M/H$. The coherence of the Knight shift and susceptibility[11] variation is apparent in the K vs $\chi = M/H$ plot (Fig. 1). The fact that the data points obtained at 1.3 K for different fields and those obtained at high temperatures lie on the same straight line demonstrates that the anomalous behavior of M/H is really due to a homogeneous band effect. This conclusion will be further supported by the analysis of the linewidth data.

As is usually done,[1,10] one can decompose the measured shift into a temperature-dependent (K^d) and a temperature-independent (K^{orb}) term, $K^d + K^{orb}$. K^d is associated with the core polarization of the inner s electrons by the d electrons, but the low value of the hyperfine constant obtained from the data[1,10] still needs theoretical justification. The constant term K^{orb} is connected to the orbital susceptibility because any direct contact contribution due to s electrons at the Fermi level is certainly negligible in view of the low s density of states on the Ti site.[12] We got $K^{orb} = 0.40 \pm 0.02$ in agreement with the earlier results.

As shown in Fig. 2 the linewidth ΔH (full width at half maximum) is proportional to $K^d H$, that is, to the magnetization when varying either the temperature (at $H = 55$ kG) or the field (at $T = 1.3$ K). In the first case a residual broadening is detected at $T > 100$ K when ΔH becomes small. First-order quadrupole effects ($I = \frac{3}{2}$ for Ti), the difference between the gyromagnetic ratio of the two Ti isotopes (i.e., ~ 20 G splitting at $H = 55$ kG), and instrumental broadening might explain the residual width. At 1.3 K slightly larger deviations from the linear dependence are observed
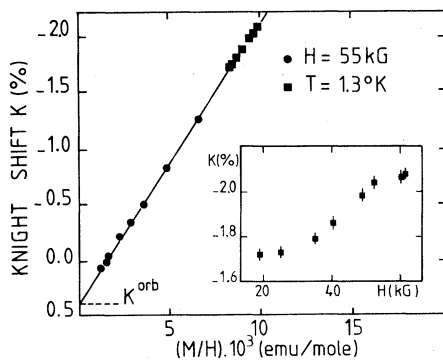
at low magnetic fields. This can be ascribed to second-order quadrupole broadening which varies as H^{-1} (the presence of inhomogeneous electric fields is further evidenced by the fact that the optimum spin echo was obtained with a $\pi/2$, $\pi/3$ pulse sequence).

To explain the observed $\Delta H \propto \chi H$ linewidth we notice that the demagnetizing field for a spherical TiBe$_2$ particle is $H' = 4\pi/3 H \chi_V = 126$ G at 60 kG, 1.3 K (i.e., at $K^d H = 1480$ G in Fig. 2). Taking into account that in a powder sample the particles have different shapes and that the dipole field due to neighboring particles has a similar magnitude, the distribution of the demagnetizing fields can account for a large part of the linewidth.[13] This means that any other line-broadening factor, such as the distribution of Knight shifts due to inhomogeneities, does not contribute more than $\Delta H/H \approx 0.03 K^d$. This limit is significantly smaller than the change of the Knight shift with field which is about $0.18 K^d$. Consequently even if the small $\chi(60)/\chi(10)$ ratio of our sample is due to inhomogeneities, the modification of the electronic states is homogeneous. We note that at 60 kG we did not see any line splitting or extra line broadening characteristic of the spin-density waves conjectured by Acker et al.[14]

For the T_1 measurements we observed the recovery of the spin echo after a saturating pulse train. This recovery was always exponential (over at least one decade). We found that at any fixed field $1/T_1 T$ is independent of the temperature between 1.3 and 4.2 K (when the Knight shift is nearly constant), showing that the relaxation
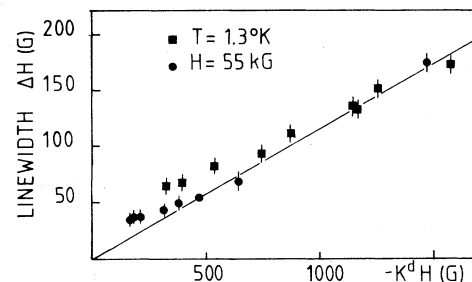

FIG. 1. Ti NMR Knight shift K vs susceptibility $\chi = M/H$. The temperature variation of K at 55 kG is plotted together with the field variation at 1.3 K. The latter is detailed in the inset.

FIG. 2. Field ($20 < H < 60$ kG, $T = 1.3$ K) and temperature ($1.3 < T < 280$ K, $H = 55$ kG) dependence of the Ti NMR linewidth ΔH plotted vs $K^d H$ which is proportional to the magnetization $M = \chi H$. The straight line with a slope of $\Delta H/H = 0.11 K^d$ is the best linear fit to the data taken at high fields and $T < 60$ K. The deviations in low fields and high temperatures are due to residual broadening (see text).

induced by any paramagnetic impurities is negligible [Fig. 3(a)]. This is supported by the fact that the low-temperature ac susceptibility in zero field did not show any Curie term characteristic of paramagnetic impurities.[11] After excluding the impurity relaxation, the measured $1/T_1 T$ can be split into a temperature-dependent and constant term $1/T_1 T = (1/T_1 T)^d + (1/T_1 T)^{orb}$, similar to the decomposition of the Knight shift. The constant $(1/T_1 T)^{orb}$ contribution is dominated by the orbital relaxation[12] and can be easily deduced from the $1/T_1 T$ vs K plot of Fig. 3(b).

The classical Korringa law states $T_1^d T (K^d)^2 = C$. The impossibility of a parabolic fit in Fig. 3 shows that this relationship is not fulfilled in $TiBe_2$. There is indeed no reason for the Korringa law to be valid because this material is far from being a simple metal. The effects of spin fluctuations have been discussed by Moriya et al.[15] for a nearly ferromagnetic Fermi liquid (and for weak intinerant ferromagnets) using a self-consistent renormalization approach. For the nearly ferromagnetic case, they found that the static susceptibility follows a Curie-Weiss law with a flattening at low temperatures, and the nuclear relaxation rate

$$\frac{1}{T_1 T} = \gamma_e^2 \gamma_n^2 k_B A_{hf}^2 \sum_q \mathrm{Im} \chi(q, \omega)/\omega$$
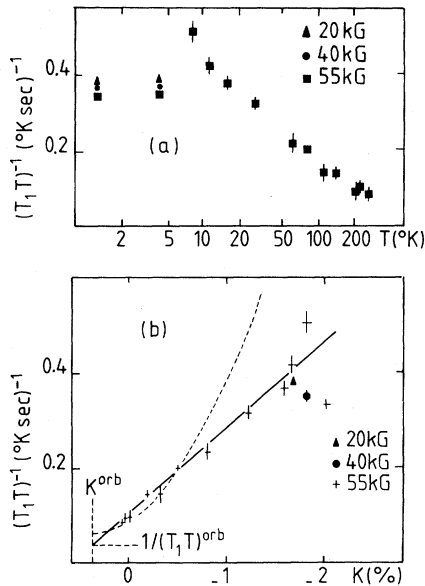

FIG. 3. The relaxation rate $1/T_1 T$ as a function of temperature (a) and Knight shift (b). The dashed line is a parabola corresponding to a Korringa law fitted to the $T > 60$ K data. The straight line is the best linear fit corresponding to Moriya's theory (see text).

is proportional to χ in low magnetic fields. Here A_{hf} is the hyperfine coupling constant and $\chi(q, \omega)$ is the dynamic susceptibility.

Our NMR measurements prove that $TiBe_2$ is a good example of this kind of behavior [Fig. 3(b)]. Indeed $1/T_1 T$ scales linearly with K^d (that is with χ), and extrapolating to $K^d \to 0$ allows one to deduce $(1/T_1 T)^{orb} = (4 \pm 1) \times 10^{-2}$ (K sec)$^{-1}$. Moriya's law is fulfilled as long as the magnetization scales linearly with the magnetic field. At 1.3 and 4.2 K, $1/T_1 T$ decreases with increasing field. The modification of the relaxation rate occurs together with the appearance of the anomalous susceptibility.

Let us consider now the magnitude of the measured relaxation rate. For a spherical band and in the limit of strong interaction the result of Moriya and Ueda[15] can be written as $1/T_1 T = (1/T_1 T)^0 3\chi/\chi^0$ where $\chi^0 = 1/2(\gamma_e \hbar)^2 \rho$ and $(1/T_1 T)^0 = \pi k_B \hbar^3 \gamma_n^2 \gamma_e^2 \rho^2 A_{hf}^2$ are the susceptibility and relaxation rate for a noninteracting electron gas and ρ is the density of states at the Fermi level for one spin direction. Using $A_{hf} = 14$ kG/μ_B as obtained from Fig. 1 and the density of states[12] $\rho = 1.38 \times 10^{12}$ states/erg, the relaxation rate $1/T_1 T = [4.58 \times 10^{-3}$ (K sec)$^{-1}] \chi/\chi^0$ is calculated and can be compared to the experimental value $1/(T_1 T)^d = [6.5 \times 10^{-3}$ (K sec)$^{-1}] \chi/\chi^0$. Although the agreement is satisfactory, this might be fortuitous as the orbital degeneracy of the d band and the real band structure have not been taken into account in these estimates. Similarly, Ueda has calculated the field variation of the relaxation rate using the magnitude of the coefficient of the M^4 term in the free energy.[16] Here again, further calculation specific to the case of $TiBe_2$, as well as experiments in higher fields, is desirable.

In conclusion the magnetic properties of $TiBe_2$ follow the behavior of a nearly ferromagnetic Fermi liquid. The dynamic properties of the susceptibility have been measured for the first time in such a system in a temperature range including the spin-fluctuation temperature T_{sf}. This allowed us to demonstrate that $(1/T_1 T)^d$ scales linearly with χ as predicted by Moriya's self-consistent treatment of the spin fluctuations. Although the macroscopic parameters of the sample studied here are not representative of the most perfect material, the magnetic properties are found to be uniform. Therefore $TiBe_2$ appears to be an excellent experimental system for studying the properties of strongly interacting Fermi liquids, as most imperfections such

as nonstoichiometry and impurities (except maybe Cu) are nonmagnetic. While they modify drastically the residual ESR linewidth and resistivity they induce rather homogeneous changes in the magnetic behavior. In particular, our results suggest that the anomaly of M/H at high H is really due to a narrow detail of the band structure[8] which can be easily smoothed out by imperfections.

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Ferroelectric Phase Transition in Microcrystals

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The ferroelectric-paraelectric phase transformation in $NaNO_2$ microcrystals (size about 5 nm) has been investigated by differential thermal analysis. Single-domain particles exhibit spontaneous polarization irrespective of their microsize. The transformation temperature, T_c, of the interior of the particles remains unaffected by their dimension, whereas T_c of the surface monolayer is lowered by a few degrees.

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The effect of a crystal's size on the temperature and/or type of a phase transition is of general interest as it illuminates the atomic interactions involved. Arguments based on energy considerations have been put forward proposing that the spontaneous polarization of isolated, freely suspended, ferroelectric crystals should cease below a certain crystal size[1]. Experimental tests of these ideas have been carried out by NMR studies of $NaNO_2$ crystals with sizes, d, ranging from 200 to 5000 nm[2]. Little effect on the phase transition has been observed. Clearly, the regime of crystal sizes well below 200 nm appears more promising for studies of size effects as surface effects become increasingly predominant. This Letter reports investigations of the phase transition of isolated $NaNO_2$ microcrystals with average sizes between 5 and 20 nm.