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LOW-TEMPERATURE DEPARTURES FROM THE KORRINGA APPROXIMATION

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## Ernest O. Lawrence Radiation Laboratory

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## LOW-TEMPERATURE DEPARTURES FROM THE KORRINGA APPROXIMATION\*

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Berkeley, California

March 1968

The recently developed NMR/ON technique<sup>1-3</sup> has made possible observations of spin-lattice relaxation for radioactive nuclei in metals at very low temperatures. Applying this technique, extended to temperatures in the 5-10 mdeg. K. range, to the system <sup>60</sup>CoFe, we have found significant deviations from the Korringa-type relation for the relaxation process. In particular, the observed relaxation time  $T_1'$  (defined below) is substantially constant below 14 mdeg. K. This phenomenon is a consequence of the Fermi-Dirac statistics obeyed by conduction electrons, and its observation thus provides additional support for the accepted model of nuclear spin-lattice relaxation through the conduction band. Close examination of the shape of the relaxation curve can yield information about the relaxation mechanism, while the exact temperature dependence of the relaxation time may permit study of the shape of the Fermi surface.

In this work we have used essentially the same NMR/ON method described previously<sup>3</sup> to obtain  $T_1'$ : nuclear orientation, detected by  $\gamma$ -ray anisotropy, was destroyed by application of rf power at the NMR frequency; the rf frequency was then shifted off resonance and the relaxation of nuclear orientation back to equilibrium with the lattice was recorded. The main changes were: (1) the present samples were prepared by melting in an atmosphere of H<sub>2</sub>, rolling to 10,000 Å, and annealing under H<sub>2</sub>, and (2) lower temperatures (as low as 5

mdeg. K.) were obtained by using a slurry of cerium magnesium nitrate and glycerol as the adiabatic demagnetization medium.  $T_1'$  was obtained by least-squares fitting the deviation of the  $\gamma$ -ray intensity along the quantization axis from its equilibrium value to the function

$$\Delta W(t) = \Delta W(0)[1 + a_1 t + a_2 \exp(-t/T_1')] .$$

Here  $t$  is the time from the beginning of relaxation, and the  $a_1 t$  term corrects for the slight warming of the sample by rf heating. The measured values of  $T_1'$  are shown in Fig. 1, plotted against  $1/T$ . Sample temperatures were monitored continuously by  $\gamma$ -ray thermometry.

To understand in simple terms why nuclear relaxation rates in metals become constant at very low temperatures, let us consider the microscopic transition probability between two magnetic substates. Magnetic-dipole relaxation is caused by off-diagonal elements of the magnetic hfs interaction  $A \vec{l} \cdot \vec{I}$ ,<sup>4</sup> in which conduction electrons individually absorb the magnetic quanta  $\gamma H$  given up by relaxing nuclei. Now let us consider some general properties of two-level systems. At equilibrium the upward and downward transition probabilities,  $W_+$  and  $W_-$ , are related by microscopic reversibility. At very low temperatures the downward probability  $W_-$  becomes constant, while the upward probability  $W_+$  approaches zero. This is analogous to the case of electromagnetic radiation: in the latter, spontaneous emission gives rise to a constant de-excitation probability in the same way that the fixed number of electron states available to relax the nuclei downward causes constant  $W_-$ . The additional emission induced by a radiation field in electromagnetic processes is paralleled by the additional number of electron states which are available at higher temperatures

due to thermal broadening of the Fermi surface. Transitions in both directions are affected equally by this additional induced rate which at high temperatures completely dominates the constant spontaneous part, i.e.,  $\frac{W_+}{W_-} \rightarrow 1$ .

Now we investigate quantitatively how  $W_{\pm}$  behave in the present case and how this affects the observed relaxation rates. We may write

$$W_{\pm} = C |\langle f | l_{\pm} | i \rangle|^2 |\langle m \mp 1 | I_{\mp} | m \rangle|^2 \times \int_0^{\infty} f(\epsilon_i) [1 - f(\epsilon_i \mp \gamma H)] d\epsilon \quad (2)$$

Here  $|i\rangle$  and  $|f\rangle$  are initial and final electron states coupled by some angular momentum operator  $l_{\pm}$ .<sup>4</sup> Quantum numbers other than  $l$  are suppressed in our notation for clarity.

The integral represents the total relative probability that an initial electron state of energy  $\epsilon_i$  will be occupied and that the final state of energy  $\epsilon_f = \epsilon_i \mp \gamma H$  will be empty.  $C$  contains all temperature-independent factors in the electron-nuclear interaction, including the density-of-states function, which is assumed to vary slowly for energy differences on the order of  $kT$ . The constancy of the effective relaxation time for low  $T$  (Fig. 1) arises from the last two factors in Eq. (2): the  $I_{\pm}$  term and the integral. Solving the integral we have (using  $\exp[-\epsilon_f/kT] \approx 0$ )

$$W_{\pm} = C |\langle f | l_{\pm} | i \rangle|^2 |\langle m \mp 1 | I_{\mp} | m \rangle|^2 \times (\mp \gamma H) \frac{e^{\frac{\mp \gamma H}{kT}}}{e^{\frac{\mp \gamma H}{kT}} - 1} \quad (3)$$

At high temperatures the last factor approaches  $kT$ , and because  $|\langle m+1 | I_+ | m \rangle|^2 = |\langle m | I_- | m+1 \rangle|^2$  the upward and downward rates between two adjacent magnetic sub-states are equal and proportional to temperature.<sup>5</sup> From the usual relation between  $W_{\pm}$  and the relaxation time for the magnetization,  $T_1$ , we can obtain the well-known Korringa dependence

$$\frac{1}{T_1} = 2C |\langle f | I_- | i \rangle|^2 kT \quad (4)$$

The only nuclear parameter in  $C$  is  $\gamma$ . Thus for a given  $\gamma$ ,  $T_1$  is independent of nuclear spin. Equation 4 is also independent of assumptions about the existence of a spin temperature.

At lower temperatures, where  $\gamma H$  is comparable with  $kT$ , the full form of the last factor in Eq. (3) must be used. This has two very important consequences. The first is that the rates up and down between two levels are no longer essentially equal but are related by

$$\frac{W_-(m \rightarrow m+1)}{W_+(m+1 \rightarrow m)} = e^{-\frac{\gamma H}{kT}} \quad (5)$$

This relation, of course, also follows from microscopic reversibility and is basic to thermal-equilibrium nuclear orientation. It is not peculiar to the use of Fermi statistics.

For a metal at low temperatures the divergence of  $W_-/W_+$  results from the sharpening of the demarcation between filled and empty electron states near the Fermi energy  $\epsilon_F$  (Fig. 2). An electron at energy  $\epsilon$  near  $\epsilon_F$  has many more empty states available at  $\epsilon + \gamma H$  (i.e., for a  $W_-$  transition) than at  $\epsilon - \gamma H$  (for a  $W_+$  transition).



The inequality between  $W_+$  and  $W_-$  precludes the use of the usual relationship  $T_1 = (\sum E_n^2) [\sum W_{mn} (E_m - E_n)^2]^{-1}$  to define  $T_1$ . The problem is further complicated because the relaxation has a time-dependence that is much more complex than a single exponential. The exact form of this time-dependence depends on nuclear spin, on assumptions about spin temperature, and on initial populations of nuclear substates. Furthermore, the quantity observed in the present work ( $\gamma$ -ray anisotropy) is not proportional to the nuclear magnetization, but to a more complicated function of the populations of the nuclear sublevels:<sup>6</sup>

$$W(\theta) = 1 + \sum_{k \text{ even}} B'_k U_k F_k P_k (\cos \theta)$$

The  $B'_k$ 's are statistical tensors describing the nuclear orientation and are functions of the nuclear spin and the populations of the magnetic substates. The  $U_k F_k$  are derived from angular momentum theory and depend on the decay scheme of the nucleus being studied. It is apparent that the values of  $T_1'$  obtained from this type of measurement will depend on the geometry of the experiment and on the nuclear decay scheme.<sup>7</sup> For all of these reasons Eq. (1) is only a first approximation to the true time-dependence of  $\Delta W(0,t)$ .

The second consequence of  $H \simeq kT$  is that  $W_+$  and  $W_-$  are no longer proportional to  $T$ . The variation of  $W_+$  and  $W_-$  with  $T$  is dependent on the statistical model involved. The proportionality of  $W_+$  and  $W_-$  to  $T$  at high temperatures follows from the Fermi statistics of conduction electrons. At low temperatures the way in which  $W_+$  and  $W_-$  depart from this  $T$  dependence is also sensitive to the statistics assumed. In a metal  $W_+$  varies faster than  $T$ ,

approaching zero as  $e^{-\frac{\gamma H}{kT}}$ , while  $W_-$  varies slower than  $T$ , becoming constant for  $kT \ll \gamma H$ . The latter result was obtained by J. A. Cameron et al.<sup>8</sup> Thus at very small  $\frac{kT}{\gamma H}$  any relaxation process, however observed, becomes temperature-independent.

The abrupt change to constant  $T_1'$  shown in Fig. 1 is a combined result of the inequality of  $W_+$  and  $W_-$  and of their different temperature dependences. This combined effect is stressed, because  $T_1'$  becomes constant at  $T \approx .014^\circ K$ , while  $\gamma H = kT$  for  $^{60}\text{CoFe}$  at  $.008^\circ K$ . At this temperature (and even below it)  $W_+$  is still sizable and  $W_-$  is still strongly temperature-dependent. Some preliminary calculations have been done to relate the measured  $T_1'$  to the reduced downward rate  $W_R$  which is the quantity represented at higher temperatures by  $C|\langle f | l_- | i \rangle|^2 kT$  in Eq. (4). These indicate the following very approximate values:

$$2 W_R = 0.70, 0.55, 0.40, \times \frac{1}{T_1'}$$

for  $1/T = 50, 100, \text{ and } 150 \text{ deg } K^{-1}$  respectively. It should be strongly emphasized that these are only valid for the case of  $^{60}\text{CoFe}$  and would be very different for other specimens, even for other Co isotopes in iron.

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FOOTNOTES AND REFERENCES

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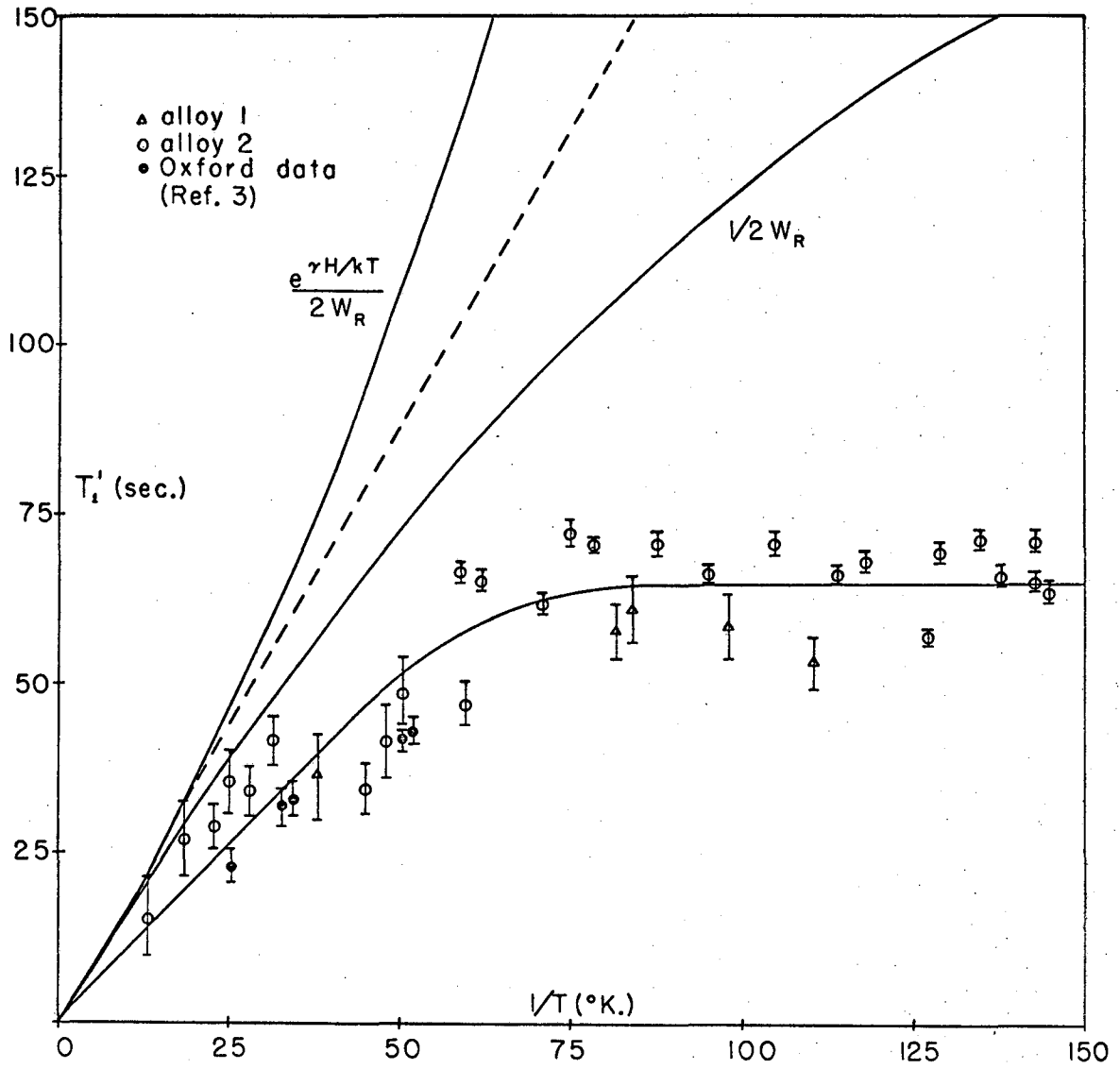
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FIGURE CAPTIONS

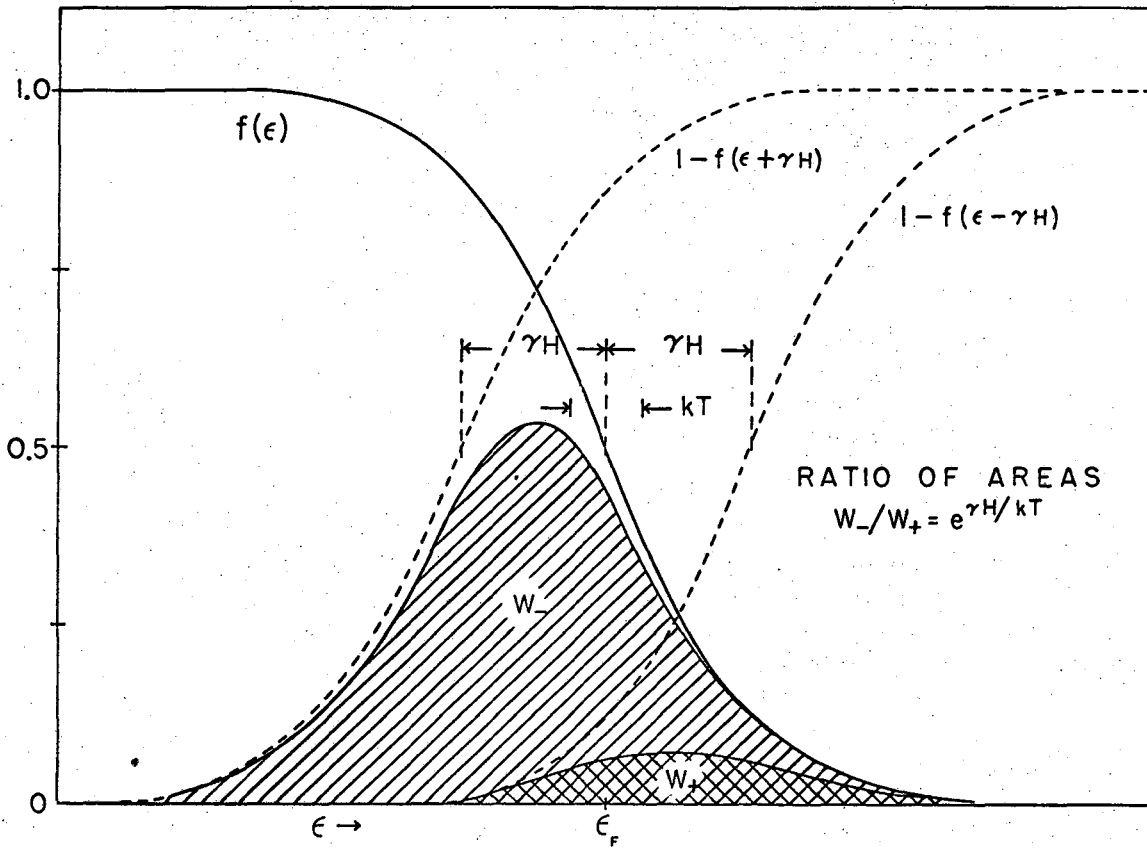
Fig. 1. Observed relaxation times  $T_1'$  vs  $1/T$ . The errors shown are one standard deviation in the fit to an exponential decay; temperature errors are approximately the diameters of plotted circles. Scatter in points is primarily a result of variations in initial conditions (rf power,  $\Delta W(0)$ , frequency modulation of rf).

Fig. 2. Fermi-Dirac distributions for filled and unfilled electronic states near the Fermi energy  $\epsilon_F$ , for  $\gamma H = 2kT$ . See Eq. (2).



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Fig. 1



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Fig. 2

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