Critical fluctuations in Ni observed with the Mössbauer effect*

M. A. Kobeissi, R. Suter, A. M. Gottlieb, and C. Hohenemser†
Department of Physics, Clark University, Worcester, Massachusetts 01610
(Received 11 November 1974)

Spin correlation times for ^{57}Fe atoms in a Ni host are derived from Mössbauer-effect line broadening. The results agree with those derived from perturbed angular correlations in *Ni* ^{100}Rh to within a factor of 2, and suggest that hyperfine correlation times in the critical region are not strongly probe dependent.

The effect of critical fluctuations in magnetic systems has been observed above the ordering temperature by hyperfine techniques and neutron scattering in both ferro- and antiferromagnetic materials. For insulating antiferromagnets such as $RbMnF_3$, MnF_2, and FeF_2, neutron-scattering results[1-3] can be understood in terms of dynamical scaling.[4] By suitable integration over q space, the neutron results can also be shown to be equivalent to the observed nuclear-resonance line broadening.[5,6] Agreement between theory, neutron scattering, and hyperfine measurements is particularly good for the case of FeF_2.[6]

In contrast, for metallic ferromagnets this satisfying state of affairs does not obtain. Neutron data are of lower quality and farther from T_C for fundamental reasons; hyperfine data are at this stage inconsistent with both theory and the neutron data.

Specifically, for Ni the neutron-scattering data[7] lie in the range $2\times10^{-2} \leq T/T_C - 1 \leq 2\times10^{-1}$, have 15–30% errors in deduced critical exponents, and if taken at face value are inconsistent with the predictions of dynamical scaling. In addition, spin-correlation times deduced from the neutron data are inconsistent with hyperfine measurements on *Ni* ^{100}Rh made by perturbed angular correlations (PAC)[8] in the range $10^{-4} \leq T/T_C - 1 \leq 10^{-2}$. The disagreement between PAC and neutron data is in both absolute magnitude and power-law behavior. Finally, correlation times deduced from Mössbauer measurements made prior to the present paper on *Ni* ^{57}Fe agree in magnitude with neither the neutron data nor the PAC data, though they show a power-law behavior that is consistent with theory.[9]

(For Fe the situation is somewhat simpler. Though neutron data are again relatively far from T_C, in the range $10^{-2} \leq T/T_C - 1 \leq 10^{-1}$, the deduced critical exponents are better defined and agree reasonably well with theory.[10] Hyperfine measurements probing the region close to T_C are not yet available.)

It is the purpose of this paper to report new Mössbauer measurements on *Ni* ^{57}Fe which show a factor-of-10–20 reduction at a given temperature in the line broadening previously reported for this system.[9] We attribute the reduction to great care in removing temperature gradients and stray magnetic fields from the source environment. The effect of the new results is to eliminate the discrepancy between *Ni* ^{57}Fe and *Ni* ^{100}Rh correlation times mentioned above.

Our experiments were done with a fixed source, mounted in an oven, and a moving absorber external to the oven. The source was produced by electroplating 1.3 mC of ^{57}Co on a 2-mm square of 99.998%-pure Ni foil, and diffusing this in a H_2 atmosphere at 1150 °C for 11 h. This produced a source which was uniformly diffused throughout the 0.0025-cm-thick foil, as could be seen from equal Fe x-ray intensities observed on either side of the foil.

When measured far above T_C the spectrum exhibited a linewidth of 0.3584 ± 0.0016 mm/sec using a $K_4Fe(CN)_6 \cdot 3H_2O$ absorber enriched to 90% in ^{57}Fe and containing 0.25 mg/cm^2 of ^{57}Fe. The observed linewidth is precisely what is expected on the basis of absorber thickness broadening[11] when the source emits a line of natural width.

The source was mounted in a vacuum furnace in which two separate heater assemblies were employed. An inner heater, constructed of BeO, sandwiched the source and two thermocouples. An outer heater, fixed with a BeO window, prevented radiation contact between the inner heater and room-temperature furnace walls. Both heaters were highly regulated, the inner through a servo system using one of the thermocouples as sensor. The measured temperature gradient between the two thermocouples in the source sandwich was ~0.04 K, and certainly less than 0.08 K.

In addition the source environment was freed of magnetic fields to a level of less than 0.2 G. This required care in designing heater windings, as well as the introduction of mumetal shielding between the Mössbauer drive and source.

Before measuring line broadening above T_C,

the Curie point was determined by two self-consistent methods as follows. (i) We measured the hyperfine field H_{hf} below T_C and from a plot of $H_{hf}^{1/\beta}$ versus T, with $\beta = 0.378 \pm 0.010$, determined the T intercept by extrapolation. This procedure is justified by the previous measurement of β in Ni ^{57}Fe by our group.[12] (ii) We measured the transmitted intensity at the centroid of the spectrum and, like others before us,[13,14] observed a sharp break in the temperature dependence of the transmission which we identified as T_C. No change in isomer shift was observed in the region of experimental interest. The results of both methods are illustrated in Fig. 1.

After the linewidth was measured above T_C, the excess width for $10^{-4} \leq T/T_C - 1 \leq 10^{-2}$ was fitted with a power law

$$\Delta\Gamma = D(T/T_C - 1)^{-n} , \quad (1)$$

in which D, T_C, and n are treated as free parameters. This yielded a third independent value of T_C. The three results for T_C are the same within statistical error and are summarized in Table I.

Since the third method, using the line-broadening data above T_C, is the most precise, the first two methods serve merely as checks of our analysis above T_C. The results for the constant D and critical exponent n derived from the fit of the data to Eq. (1) are

$$D = (0.24 \pm 0.13) \times 10^{-4} \text{ mm/sec} , \quad n = 0.71 \pm 0.24 . \quad (2)$$

The line broadening as a function of temperature and reduced temperature is given in Table II. Examples of spectra fitted with a Lorentzian line shape are shown in Fig. 2. The latter indicates that Lorentzians fit well to all the data above T_C, but fail abruptly even a small distance below T_C. To illustrate the dramatic reduction in the broadening at a given temperature, the data are plotted together with the earlier results of Gumprecht *et al.*[9] in Fig. 3.

To test whether our precautions with the source environment are in fact responsible for the reduced broadening observed, we reintroduced small applied magnetic fields and temperature gradients. External fields up to 4 G in magnitude, applied parallel to the source foil, yielded measurable deviations from shielded-source data only for $T/T_C - 1 < 10^{-4}$, and suggest that small magnetic fields did not play a role in the larger broadening observed in earlier work.[9] On the other hand, results for temperature gradients of 0.7 °C, shown in Fig. 3, suggest that temperature gradi-

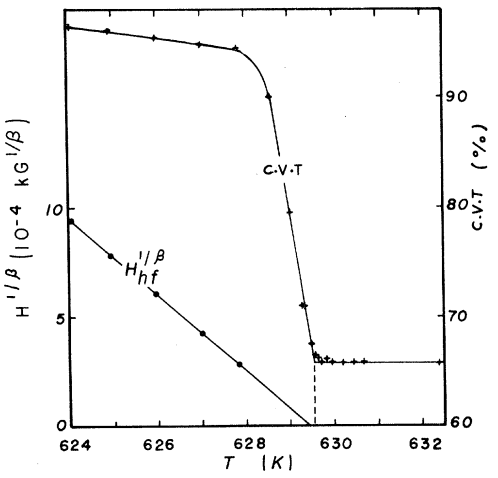

FIG. 1. Determination of T_C by two methods. The lower curve shows $H_{hf}^{1/\beta}$ vs T for $\beta = 0.378$, and indicates T_C as the T intercept. The upper curve shows the centroid-velocity transmission (CVT) vs T, and indicates T_C by a break in the curve. The values of T_C obtained in the two cases are given in Table I.

TABLE I. Experimental T_C values.

Method	T_C (K)
$H_{hf}(T)$, $T < T_C$	629.44 ± 0.10
Thermal scan	629.55 ± 0.07
$\Delta\Gamma(T)$, $T > T_C$	629.54 ± 0.04

TABLE II. Excess linewidth above T_C.

T (K)[a]	$(T - T_C)/T_C$[b]	$\Delta\Gamma$ (10^{-3} mm/sec)[c]
629.62	1.27×10^{-4}	15.19
629.64	1.54×10^{-4}	13.91
629.66	1.90×10^{-4}	9.63
629.68	2.14×10^{-4}	9.02
629.70	2.54×10^{-4}	11.80
629.72	2.85×10^{-4}	10.09
629.74	3.17×10^{-4}	6.00
629.78	3.73×10^{-4}	8.57
629.80	4.05×10^{-4}	4.42
629.85	4.92×10^{-4}	5.33
629.87	5.24×10^{-4}	4.98
629.93	6.19×10^{-4}	4.28
630.00	7.30×10^{-4}	5.04
630.07	8.44×10^{-4}	3.85
630.20	1.05×10^{-3}	1.98
630.45	1.44×10^{-3}	0.84
630.65	1.76×10^{-3}	2.15
632.40	4.54×10^{-3}	−1.02
635.57	9.58×10^{-3}	0.60
664.15	5.50×10^{-2}	0.00[d]

[a] Error is 0.02 K for each point.
[b] Error is 1.1×10^{-4} for each point.
[c] Error is 3.2×10^{-3} mm/sec for each point.
[d] $\Delta\Gamma$ is *defined* to be zero for this temperature.

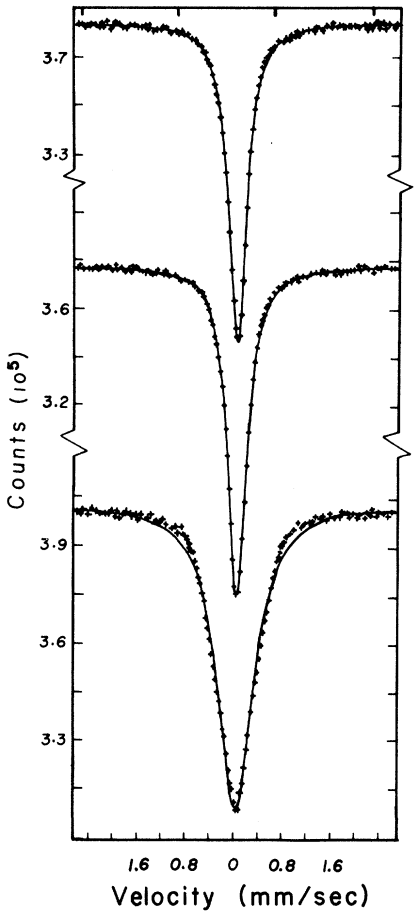

FIG. 2. Illustration of Lorentzian fits to the data above and below T_C. Top: $T-T_C=0.46$ K; middle: $T-T_C=0.06$ K; bottom: $T-T_C=-0.52$ K. Notice that the Lorentzian fit fails only for $T<T_C$, as expected.

ents can probably account for most of the larger line broadening seen in the earlier work.[9]

To compare the new results with neutron scattering[7] and perturbed-angular-correlation data on *Ni* ^{100}Rh,[8] we have calculated spin-correlation times according to the theory of Bradford and Marshall.[15] These authors treat a hyperfine Hamiltonian

$$\mathcal{H}=A_\alpha \vec{I}_\alpha \cdot \vec{S}(t), \quad \alpha=e,g \tag{3}$$

where e and g denote the excited and ground state, respectively, and $\vec{I}$ and $\vec{S}(t)$ are the nuclear and electronic spin. The use of this Hamiltonian implicitly assumes that the hyperfine field at the ^{57}Fe nucleus is produced entirely by the localized electronic spin $\vec{S}(t)$, i.e., $\vec{H}_{\rm hf}(t)\propto\vec{S}(t)$. That this is at least approximately true follows from the study of hyperfine field systematics in ferromagnetic hosts.[16]

The basic assumptions of the Bradford-Marshall theory are as follows. (a) The fluctuations are isotropic. (b) The inequalities $\tau_z\omega_L\ll 1$, $\tau_z\Delta\Gamma\ll 1$, and $\Delta\Gamma/\omega_L\ll 1$ hold, where τ_z is the correlation time for one component of $\vec{S}$, ω_L is the nuclear Larmor frequency, and $\Delta\Gamma$ is the full excess width expressed in sec^{-1}. (c) The correlation function is exponential. Condition (a) has been demonstrated to be correct by two of the present authors.[8] That the restricting inequalities hold is seen from Table III. Condition (c) does not apply for critical fluctuations.[8] However, it may be shown that the final formula of the theory is unaltered if a correlation function of general form is introduced and the integral definition of τ_z is used, i.e.,

$$\tau_z=\tfrac{1}{2}\int_{-\infty}^{\infty}[G^{zz}(t)/G^{zz}(0)]\,dt\,. \tag{4}$$

To first order, Bradford and Marshall obtain a Lorentzian line shape of full width,

$$\Gamma=\Gamma_n+\Delta\Gamma\,, \tag{5}$$

where Γ_n is the natural width and $\Delta\Gamma$ is the excess width which we have derived from experiment, and and which is related to the correlation time through

$$\Delta\Gamma(\text{sec}^{-1})=\tau_z[2S(S+1)/3\hbar^2](\tfrac{15}{4}A_e^2-\tfrac{5}{2}A_eA_g+\tfrac{3}{4}A_g^2)\,. \tag{6}$$

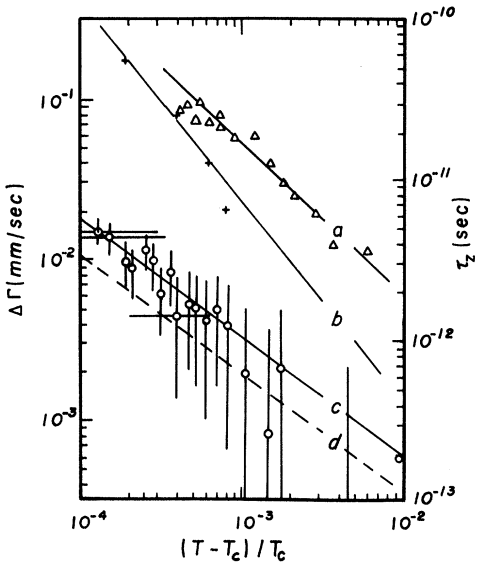

FIG. 3. Line broadening and corresponding autocorrelation times calculated with the theory of Bradford and Marshall. (a) *Ni* ^{57}Fe data of Ref. 9 (error bars suppressed); (b) this work, with purposely large temperature gradient of 0.7 K (error bars suppressed); (c) this work, with temperature gradient of ~0.04 K; (d) fit obtained for PAC data on *Ni* ^{100}Rh, Ref. 8 (right-hand scale only applies).

TABLE III. Restricting inequalities.

Inequality	Maximum value
$\tau_z \omega_L \ll 1$	3×10^{-3}
$\tau_z \Delta\Gamma \ll 1$	3×10^{-5}
$\Delta\Gamma/\omega_L \ll 1$	1×10^{-2}

To obtain the hyperfine coupling constants we have used the relations

$$A_\alpha = \gamma_\alpha H_0/S, \quad \alpha = e, g \tag{7}$$

where $\gamma_e = -0.050$ and $\gamma_g = 0.089$ are gyromagnetic ratios and $H_0 = 280$ kG is the average hyperfine field measured at 0 K. With this we find

$$\Delta\Gamma(\text{sec}^{-1}) = 1.49\times10^{11}[(S+1)/S]\tau_z \ . \tag{8}$$

When this is converted to velocity units $[\Delta\Gamma(\text{sec}^{-1}) = 7.30\times10^{7}\Delta\Gamma(\text{mm/sec})]$, and with $S = \frac{3}{2}$, as is appropriate for Fe, we obtain the useful result

$$\tau_z(\text{sec}) = 2.94\times10^{-10}\Delta\Gamma(\text{mm/sec}) \ . \tag{9}$$

The correlation times calculated with this formula can be read from Fig. 3 by use of the right-hand scale. For comparison, correlation times derived for[8] Ni^{100}Rh are shown by a broken line. It is seen that the results for Ni^{57}Fe and Ni^{100}Rh now agree to within a factor of 2 in absolute magnitude, and to within statistics in the derived power-law dependence.

One serious question that remains for both systems is whether the observed relaxation effects can be further reduced by additional improvements in source environment. We believe the effects are indeed irreducible, and we base our belief on the fact that several runs with somewhat different conditions and, for Ni^{100}Rh, different sources gave essentially identical results.

Aside from this, it is worth emphasizing the entirely predictable but little-noticed fact that weaker hyperfine coupling leads to a smaller region in which critical fluctuations are observable. Whether measured by perturbed angular correlations or Mössbauer effect, the nuclear relaxation rate (line broadening) depends on $(\gamma H_0)^2$. For Ni^{57}Fe this quantity is 300 times smaller than for Ni^{100}Rh, if we ignore for a moment the small difference in excited and ground-state moments in ^{57}Fe. It is for this reason that, in comparison to Ni^{100}Rh, more care must be taken with the source environment; and it is only because small linewidth effects are far easier to detect than equivalent perturbed-angular-correlation relaxation that the Ni^{57}Fe experiment produces interpretable results at all.

Finally, and most important, the present results reinforce the discrepancy between neutron-scattering data and hyperfine results that were noted in the work on Ni^{100}Rh. The explanation of the discrepancy remains unclear, though it is fairly certain that one or more of the following apply.

(i) The form of the Van Hove scattering function, $S(\vec{q}, \omega)$, used to fit the neutron data is not valid near the origin of $(\vec{q}, \omega)$ space, which is the region predominantly sampled by hyperfine experiments.

(ii) The neutron results, which were assumed to be hydrodynamic in character[7] and were fitted with the hydrodynamic form of $S(\vec{q}, \omega)$, were in fact not. This is possible because of the considerable scatter of the data in these rather difficult experiments.

(iii) There is something fundamentally wrong with the interpretation of the hyperfine data using a local-moment picture for the probe spin.

A fourth possibility, namely, that hyperfine results are strongly probe dependent, seems to be unlikely in view of the agreement between derived correlation times for Ni^{100}Rh and Ni^{57}Fe.

The authors thank Dr. Pierre C. Hohenberg for helpful critical comments on the manuscript and E. Rolfe for experimental assistance in the early stages of the work.

*Research supported in part by the National Science Foundation and the Research Corporation.

†During 1973–74, guest of the Laboratorium voor Algemene Natuurkunde, University of Groningen, Netherlands, with a stipend from "Stichting voor Fundamenteel Onderzoek der Materie" (FOM).

[1]R. Nathans, F. Menzinger, and S. J. Pickart, J. Appl. Phys. 39, 1237 (1968).

[2]M. P. Schulhof, P. Heller, R. Nathans, and A. Linz, Phys. Rev. Lett. 24, 1184 (1970); Phys. Rev. 131, 2304 (1971).

[3]M. P. Schulhof, M. T. Hutchings, and H. J. Guggenheim, J. Appl. Phys. 42, 1376 (1971).

[4]B. I. Halperin and P. C. Hohenberg, Phys. Rev. 177, 952 (1969).

[5]P. Heller, in *Critical Phenomena*, Natl. Bur. Std. Misc. Publ. No. 273 (U.S. GPO, Washington, D.C., 1966), p. 58.

[6]A. M. Gottlieb and P. Heller, Phys. Rev. B 3, 3615 (1971).

[7]V. J. Minkiewicz, M. F. Collins, R. Nathans, and G. Shirane, Phys. Rev. 182, 624 (1969).

[8]A. M. Gottlieb and C. Hohenemser, Phys. Rev. Lett. 31, 1222 (1973).

[9]D. Gumprecht, P. Steiner, G. Crecelius, and S. Hüfner, Phys. Lett. A 34, 79 (1971).

[10]M. F. Collins, V. J. Minkiewicz, R. Nathans, L. Passell, and G. Shirane, Phys. Rev. 179, 417 (1969).

[11]S. Margulies and J. R. Ehrmann, Nucl. Instr. 12, 131 (1961).
[12]H. C. Benski, R. C. Reno, C. Hohenemser, R. Lyons, and C. Abeledo, Phys. Rev. B 6, 4266 (1972).
[13]R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. 128, 2207 (1962).
[14]D. G. Howard, B. D. Dunlap, and J. G. Dash, Phys. Rev. Lett. 13, 752 (1964).
[15]E. Bradford and W. Marshall, Proc. Phys. Soc. Lond. 87, 731 (1966).
[16]D. A. Shirley, S. S. Rosenblum, and E. Matthias, Phys. Rev. 170, 363 (1968).