

Time-Differential Perturbed Angular Correlations on ^{57}Fe in Cu-Ni Alloys: Mössbauer Doublets Explained*

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It is shown that when hyperfine interactions at ^{57}Fe nuclei are studied by both Mössbauer effect and time-differential perturbed angular correlations, information is obtained which is unavailable from either technique alone. In particular, previous ambiguities in the interpretation of ^{57}Fe Mössbauer spectra of Cu-Ni alloys are removed: The Mössbauer doublet is shown to be primarily due to a distribution of electric field gradients acting on the ^{57}Fe nuclei.

The resolution of the Mössbauer-effect (ME) technique is limited, through the uncertainty principle, by the lifetime of the nuclear excited state. For ME spectra with unresolved or just barely resolved structure, it is not possible to establish the broadening mechanism (i.e., magnetic, quadrupole, isomer shift, or some combination of these) on the basis of the ME spectra alone. It is the purpose of this Letter to show that the application of time-differential perturbed angular correlations (TDPAC) to the study of such cases can *unambiguously* determine the origin of the hyperfine interaction when combined with existing Mössbauer data. This technique is applied to determine the origin of the broadened lines in the ^{57}Fe ME spectra of Cu-rich Cu-Ni alloys containing Fe impurities.

The recent development¹⁻³ of first-photoelectron triggering with NaI(Tl) counters has made possible TDPAC measurements using ^{57}Fe . This technique is capable of greater resolution than the ME primarily for two reasons: (1) ME has lifetime broadening from both a source and an absorber whereas TDPAC utilizes only a source; (2) TDPAC is not affected by an isomer shift. Given sufficient a signal-to-noise ratio, either technique alone could, *in principle*, distinguish a pure single-valued quadrupole from a pure single-valued magnetic broadening. However, a slight distribution of either prevents the distinction from being made unambiguously. A combination of data from both techniques provides the necessary information to make such a distinction.

The broadened ME lines observed⁴ in Cu-Ni alloys containing dilute Fe impurities were later shown^{5,6} to be barely resolved doublets. The existence of these doublets has interesting consequences for any assumed line-broadening mechanism such as magnetic hyperfine field, electric field gradient, or isomer shift. Although it was

realized that no rigorous proof of the doublet origin existed, some of the interesting consequences of a magnetic origin for the doublet structure were explored.⁷ On the other hand, it has been assumed in subsequent studies^{8,9} that the broadening is characteristic of an electric quadrupole interaction as originally proposed.⁴ The third possibility, i.e., that the broadening is due to ^{57}Fe atoms in different environments which yield different isomer shifts, has generally been ruled out^{4,6} on the basis of behavior with Ni concentration. Again, no real disproof of this third possibility had yet been obtained.

It is useful to compare the expressions for the Mössbauer and TDPAC spectra in the two limits of pure quadrupole and pure magnetic interaction. The well-known Mössbauer spectrum consists of a set of Lorentzian-shaped lines whose number and splittings are determined by the type and strength of the hyperfine field. For ^{57}Fe , a quadrupole interaction results in a two-line spectrum with a splitting given by

$$\Delta E = \frac{1}{2}e^2Qq(1 + \frac{1}{3}\eta^2)^{1/2}, \quad (1)$$

where Q is the nuclear quadrupole moment, eq is the z component of the electric field gradient (EFG), and η is the asymmetry parameter. A magnetic interaction gives rise to a six-line spectrum where the outer line splitting for ^{57}Fe is given by

$$\Delta_{1,6} = (3|g_0| + |g_1|)\mu_N H_{\text{hf}}, \quad (2)$$

where g_0 and g_1 are the ground- and excited-state g factors, μ_N the nuclear magneton, and H_{hf} the magnetic hyperfine field. The problem in interpreting Mössbauer spectra arises when the above splittings are of the same size as the Mössbauer linewidth (as is the case for ^{57}Fe in Cu-Ni). The two types of spectra, in this case, appear quite similar (see Fig. 1).

The Mössbauer spectra should be compared with the corresponding TDPAC spectra for the same two field cases. The TDPAC attenuation factors $G_2(t)$ for polycrystalline samples for the types of interactions under consideration are as follows¹⁰:

$$G_2(t) = \frac{1}{5}(1 + 4 \cos \omega_0 t),$$

$$\hbar \omega_0 = \frac{1}{2} e^2 q Q (1 + \frac{1}{3} \eta^2)^{1/2},$$
(3)

for a pure quadrupole interaction and

$$G_2(t) = \frac{1}{5}(1 + 2 \cos \omega_L t + 2 \cos 2\omega_L t),$$

$$\hbar \omega_L = g_1 \mu_N H_{\text{hf}}$$
(4)

for a pure magnetic interaction. These two $G_2(t)$'s are also shown in Fig. 1 with the frequencies calculated from the corresponding Mössbauer spectra. Note that while the two Mössbauer spectra are nearly identical, the corresponding TDPAC differ significantly in both form and frequency. This suggests two ways of utilizing TDPAC data on ⁵⁷Fe in Cu-Ni alloys to determine the origin of the field. If used in conjunction with existing Mössbauer data, it is only necessary to extract a frequency from the TDPAC data to arrive at an unambiguous determination of the interaction type. If, however, TDPAC da-

ta alone are used to determine the type of hyperfine interaction, then the overall shape of the TDPAC spectrum is needed, and this, as will become clear later, cannot be determined with as much confidence as a fundamental frequency. Note that if the ME doublet were due to an isomer-shift mechanism alone, *no* oscillations would be observed in the TDPAC data. In the presence of a distribution of fields, comparison of the two sets of data can be used to set limits on the amount of isomer-shift broadening in the ME spectrum.

A source was prepared by diffusing several millicuries of ⁵⁷Co into a 25- μ m-thick foil of Cu_{0.53}Ni_{0.47} at 900°C for several minutes, followed by a rapid quench. A small piece ($\sim 3 \mu$ Ci) was removed for the TDPAC measurements and the remainder used for Mössbauer measurements. A single-line absorber of potassium ferrocyanide was utilized. This absorber exhibited a linewidth of 0.26 mm/sec against a (⁵⁷Co)Pd source. A room-temperature spectrum obtained with this absorber and the (⁵⁷Co)Cu_{0.53}Ni_{0.47} source is shown in Fig. 2. This spectrum was fitted¹¹ by least squares with three models: (1) a six-line magnetic hyperfine field pattern with the full width at half-maximum (Γ) of all lines constrained to be equal (a very small amount of admixed quadrupole effect was used to reproduce the asymmetry evident in the spectrum of Fig. 2), (2) a two-line pattern characteristic of a quadrupole effect, and (3) a Gaussian distribution of quadrupole doublets, with the probability p of a given quadrupole

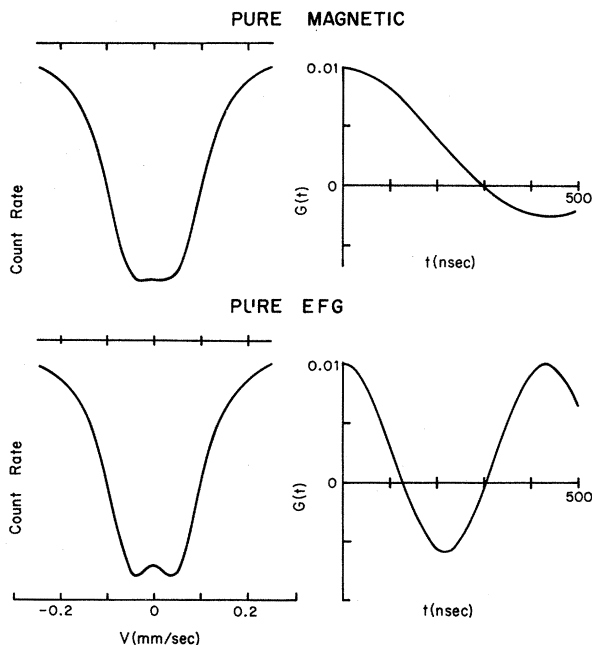


FIG. 1. Theoretical Mössbauer spectra and the corresponding ⁵⁷Fe TDPAC spectra for the two cases of pure quadrupole and pure magnetic interactions. The Mössbauer parameters for the magnetic spectrum are $\Delta_{1,6} = 0.275$ mm/sec, $\Gamma = 0.24$ mm/sec; for the EFG spectrum, $\Delta E = 0.20$ mm/sec, $\Gamma = 0.26$ mm/sec.

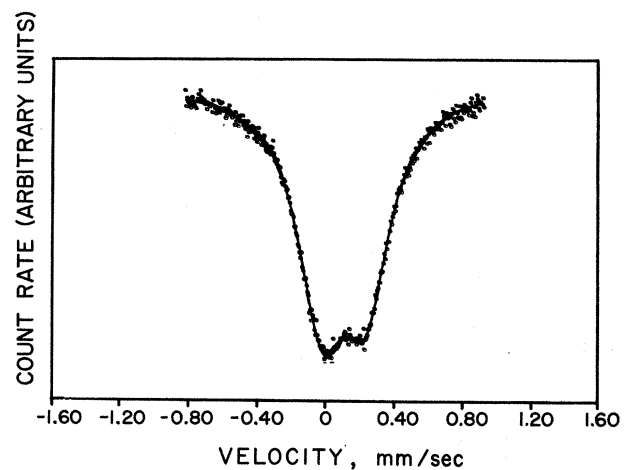


FIG. 2. Room-temperature Mössbauer-effect spectrum of (⁵⁷Co)Cu_{0.53}Ni_{0.47} versus a potassium ferrocyanide absorber. Dots, data points; solid line, limits of the three least-squares fits described in the text.

TABLE I. Parameters obtained by least-squares fitting the spectrum of Fig. 2 with the three models described in the text. The listed errors are estimated uncertainties.

Model	Γ (mm/sec)	ΔE (mm/sec)	H_{hf} (kG)	σ_E (mm/sec)	χ^2 per point
(1)	0.27 ± 0.02	0.005	11.0 ± 0.05	...	1.26
(2)	0.35 ± 0.02	0.26 ± 0.02	1.21
(3)	0.26^a	0.26 ± 0.02	...	0.12 ± 0.02	1.19

^aThis value was constrained during the least-squares fit.

splitting given by

$$p(\Delta E) \propto \exp[-(\Delta E - \Delta E_0)^2 / 2\sigma_E^2]. \quad (5)$$

The theoretical spectra obtained by these three techniques all fit within the solid curve superimposed on the data in Fig. 2. The parameters obtained are given in Table I. The χ^2 per datum point are also listed in Table I.

The TDPAC experiment was performed on a small piece ($\sim 3 \mu\text{Ci}$) taken from the $(^{57}\text{Co})\text{Cu}_{0.53}\text{Ni}_{0.47}$ ME source. The PAC spectrometer used was a three-counter slow-fast delayed-coincidence apparatus similar in most respects to the one used in previous ^{57}Fe TDPAC measurements³ on pure Ni. Because of the extremely small anisotropy for the 122–14-keV cascade in ^{57}Fe ($A_2 \approx -0.02$),³ care had to be taken to remove all instrumental effects which might have resulted in a time-dependent baseline. Spectrometer linearity was checked using 3- μCi sources of ^{57}Co in Ni and Pd. Data were taken simultaneously at angles of $\pi/2$ and π and were reduced in the following way:

$$R(t) = \frac{C(\pi/2, t) - C(\pi, t)}{C(\pi/2, t) + C(\pi, t) - 2B}, \quad (6)$$

where $C(t)$ is the time-dependent coincidence rate given by¹⁰

$$C(\theta, t) = N_0 \exp(-t/\tau_N) [1 + P_2(\cos\theta)A_2G_2(t)] \quad (7)$$

and $G_2(t)$ is given by Eq. (3) or (4), depending on the type of interaction. For the choice of angles indicated, the quantity $R(t)$, to first order, is then seen to be given by

$$R(t) = -\frac{3}{4}A_2G_2(t). \quad (8)$$

Reduced data for the Cu-Ni alloy are shown in Fig. 3, and represent a 15-day continuous run. The data were fitted by least squares with two forms:

(1) $R(t) = A \exp(-t^2\sigma^2/2) \cos\omega_0 t$, corresponding to a distribution of EFG's as in Eq. (5). The re-

sults were $\omega_0 = 15.7 \pm 1.6$ MHz and $\sigma = 8.0 \pm 1.6$ MHz which, when converted into ME parameters, give $\Delta_E = 0.214 \pm 0.020$ mm/sec and $\sigma_E = 0.11 \pm 0.02$ mm/sec.

(2) $R(t) = A(\cos\omega_L t + \cos 2\omega_L t)$, corresponding to a single magnetic hyperfine field. The result was $\omega_L = 11.7 \pm 0.3$ MHz, which corresponds to a magnetic hyperfine field of $H_{\text{hf}} = 23.8 \pm 0.6$ kG.

Comparing the above results with models (1) and (3) in Table I, it is clear that ME and TDPAC results are consistent when the EFG case is assumed, and inconsistent when the magnetic hyperfine case is assumed, thereby ruling out the latter as the primary source of the ME doublet. The possibility that the ME spectrum consists of two separate lines with different isomer shifts is also ruled out since this model would have resulted in a null TDPAC spectrum.

The conclusion reached, therefore, is that the combination of ME and TDPAC data determines the environment of Fe nuclei in Cu-Ni alloys to be primarily due to an electric quadrupole interaction. The amplitude of the TDPAC spectrum,

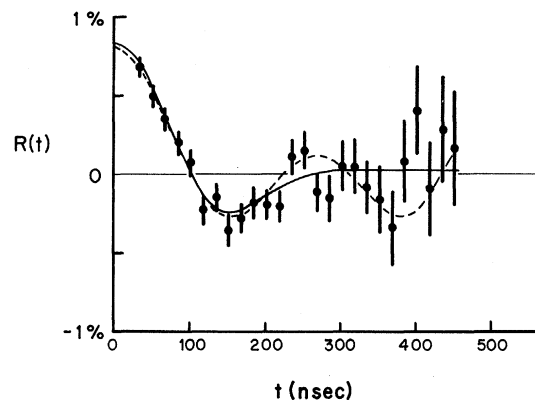


FIG. 3. Room-temperature TDPAC spectrum for ^{57}Fe in $\text{Cu}_{0.53}\text{Ni}_{0.47}$. Solid line, least-squares fit to a distribution of EFG's; dashed line, fit to a single magnetic hyperfine field. As with the Mössbauer spectrum, both fits are equally good given the quality of the data.

when corrected for geometrical attenuation, gives an anisotropy A_2 of 0.019, thereby indicating that most if not all ^{57}Fe nuclei in the alloy experience the quadrupole interaction. The loss of coherence in the PAC spectrum can best be explained by a distribution of EFG magnitudes with $\sigma_E = 0.11 \pm 0.02$ mm/sec, thereby accounting for the additional Mössbauer broadening. It is also possible to explain the loss of coherence as due to small magnetic fields, less than 3 kG, mixed with the basic EFG. The agreement between field-spread values σ_E deduced from each set of data shows that there is little room for additional broadening in the Mössbauer spectrum due to isomer shifts. Although a rather large variation of near-neighbor environments appears necessary to explain the field distribution, the isomer shift is apparently little affected by such changes in the near-neighbor environment.

We have shown that TDPAC measurements on ^{57}Fe can be quite useful in interpreting unresolved Mössbauer spectra. The limitations imposed by the small anisotropy of the cascade can be overcome, in many cases, by the use of properly designed multicounter NaI(Tl) spectrometers. Several other applications of the technique come to mind, e.g., the determination of the origin of broadened Mössbauer singlets in disordered alloys such as stainless steel. The techniques may also prove useful in extending the range of possible experiments to materials where low recoilless fractions have made ME measurements diffi-

cult or impossible.

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Critical Asymmetry in Local Fluctuations in SrTiO_3 for $T \rightarrow T_c^-$

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A critical asymmetry in local fluctuations of the rotational parameter φ in SrTiO_3 for $T < T_c$ and $\langle \varphi \rangle \neq 0$ is observed directly by the asymmetry a_s of the paramagnetic resonance lines of $\text{Fe}^{3+}-V_O$ pair centers. The parameter a_s increases in a critical manner for $T \rightarrow T_c^-$. It is postulated that such an asymmetry is a general property of second-order phase transitions.

In this Letter we describe a novel phenomenon in the critical behavior of a crystalline solid undergoing a distortive phase transition¹ of second order. It occurs below the phase transition where the (generalized) order parameter $\langle \varphi \rangle$ is nonzero, and consists of an asymmetry in the local fluctuations $\delta\varphi_i$ around the value φ_i^m at which the probability $P(\varphi_i)$ to observe φ_i is a maximum,

i.e., if $\langle \varphi \rangle \neq 0$, then odd moments in $\varphi_i - \varphi_i^m$ also differ from zero. This asymmetry increases in a critical manner for $T \rightarrow T_c^-$. Its presence is directly observed by the asymmetry of $\text{Fe}^{3+}-V_O$ pair paramagnetic resonance lines. It is postulated that this broken symmetry of local fluctuations for nonzero order parameter occurs quite generally.