Small-angle scattering of Mössbauer γ rays near magnetic phase transitions

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The small-angle scattering of Mössbauer γ rays of the canted antiferromagnet FeF_3, the ferromagnet Fe_3C, and the ferromagnetic alloy Ni + 2-at.%. Fe^{57} was studied as a function of the ambient temperature. A pronounced increase in the small-angle scattering of the recoilless 14.4-keV γ rays of these substances is observed as the temperature increases toward T_c. This phenomenon exhibits features similar to those which were observed by x-ray scattering of binary alloys, light scattered by fluids, and neutrons of ferromagnets in the neighborhood of the critical temperature. The scattering intensity begins to increase around $0.9T_c$ where the Mössbauer spectrum shows a central peak coexisting with hyperfine splitting. The critical scattering is angle dependent and suggests a relation between the "superparamagnetic."-type coherent spin fluctuations suggested in the literature and the onset of criticality near second-order magnetic phase transitions.

I. INTRODUCTION

The critical region near a second-order magnetic phase transition is marked by a great increase in the large-scale fluctuations of various parameters of the material. This leads to a sharp increase in the intensity of light[1,2] in x-ray[3] and neutron[4] small-angle scattering by such fluctuations. Recently there has been considerable interest in problems associated with electron-spin relaxation in Mössbauer spectroscopy of ordered magnetic systems[5-9] in the temperature region in which the presence of a central "paramagnetic" peak and a hyperfine splitting (ordered state) can simultaneously be discerned. However, the small-angle critical scattering was not studied in these experiments.

In this experiment we attempted to measure the small-angle critical scattering of the γ rays (emitted from a paramagnetic Mössbauer Co^{57} source) of some magnetically ordered iron compounds, simultaneously with a measurement of the Mössbauer spectrum. The appearance of the central peak in the spectrum near the critical temperature T_c is observed as being correlated with the critical scattering by collective spin fluctuations related to small domains in the material.

The small-angle critical Mössbauer scattering of FeF_3, Fe_3C, and iron-nickel alloy are discussed in this report.

II. EXPERIMENTAL DETAILS

(a) *Samples*. The source used throughout the experiments was a 25-mCi Cu : Co^{57}. For absorbers we used a powdered FeF_3 (canted antiferromagnet) of an effective thickness $t = 3$ and a Néel temperature $T_N = 362\,^\circ K$, encapsulated in epoxy. The cementite, Fe_3C (a ferromagnet with $T_C = 478\,^\circ K$) was extracted from a low-carbon steel in the usual way[10-14] and used as a powdered ab-

sorber of $t = 3$, encapsulated on a disk-shaped porcelain cement. Here $t = n\sigma_0 f$, where n is the amount of resonant nuclei per cm^2 of the absorber, σ_0 is the on-resonance cross section, and f is the Mössbauer fraction. An alloy of 2-at.% Fe^{57} in nickel ($T_C = 663\,^\circ K$) foil was studied as an absorber of $t = 10$. For the purpose of comparison a pure nickel ($T_C = 663\,^\circ K$) foil with the same thickness and size was studied.

(b) *Temperature media*. For the FeF_3, a commercial cryo-oven (RICOR MCH-5B) was used. The temperature was regulated by a gold-iron versus Chromel-P thermocouple, servo-controlling the flow of liquid nitrogen against a heater. The temperature of the sample could be kept constant within $\pm 0.05\,^\circ K$ during run times. For the other samples a vacuum oven was used. The heater and sample temperatures were regulated and measured by two separate Chromel-Alumel thermocouples, with temperature stability of $\pm 0.2\,^\circ K$. In each of the cryo-ovens, three thermal radiation gold-plated shields enclosed the sample. The windows were made of gold-plated Mylar for the cryo-oven and thin gold-plated aluminum foils for the inner windows and Mylar on the outside. The samples were plated with thin aluminum layers. The temperatures were recorded by a null potentiometer relative to ice-water reference.

(c) *Spectrometer*. An on-line spectrometer operating on a constant acceleration mode accumulated and recorded the velocity spectra. Paralleling with the accumulation of the counting rate versus Doppler velocity spectrum by the computer, the count-rate yield of the single-channel pulse-height analyzer was recorded for each temperature of the sample and for each scattering angle by a scaler for preset times of 15 min. The scaler clock is a crystal oscillator of 10^4 Hz. The total count rate is referred to in the text as the "integral scattering intensity." The spectra were analyzed

by a nonlinear least-squares program, assuming Lorentzians.

(d) *Background corrections.* Three types of background corrections must be made: (1) For an absorber of a finite thickness the total spectral area is reduced as T_c is approached, due to an increasing overlap of the six magnetic nuclear transitions, reaching a minimum at T_c. This is the saturation effect (or, multiple scattering[15]). Thus, the total transmitted count rate increases to its maximum accordingly. This effect is negligible for thin absorbers. (2) There is a temperature-dependent reduction in the total spectral area with the increasing sample temperature due to the temperature dependence of the Mössbauer f factor, resulting in an appropriate increase in the total count rate. For polycrystals these effects are independent of the scattering angle. The integral scattered intensity was measured versus the ambient temperature through an iris with a 20° opening (which is a rather large angle for observation of any substantial critical effects), in order to observe these effects and thus eliminate them. (3) Background corrections: In the absence of a source, the "true" background of ~70 counts per 15 min was measured by shielding the 0.015-in.-thick NaI(Tl) crystal detector with lead. The stabilized single-channel analyzer was set to include most of the 14.4-keV peak. The resolution of our detector is sufficient to separate the ~6-keV x-rays of the iron from the 14.4-keV γ's. Our source has no other troublesome x rays. A sufficiently large ratio of the photoelectric to Compton cross section gives negligible effects of Compton scattering in the source. A filter of 0.005 in. of brass allows the passage of less than 0.02% of the 14.4-keV γ's, while it removes only ~4% of the high-energy γ's. After the experimental arrangement was completed the filter was placed between the Mössbauer absorber and the detector.
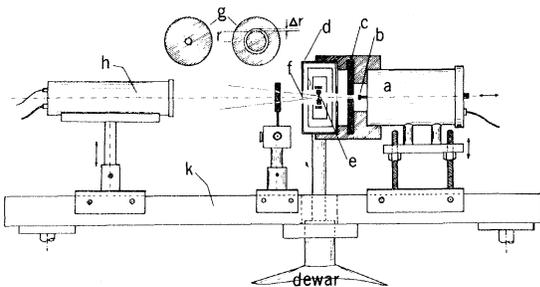
FIG. 1. A sketch of the experimental arrangement: (a) transducer; (b) source, (c) fixed lead colimator to source; (d) oven-cryostat; (e) absorber; (f) window; (g) scattering-angle lead iris, on variable mirror mount; (h) scintilator; (k) optical bench.
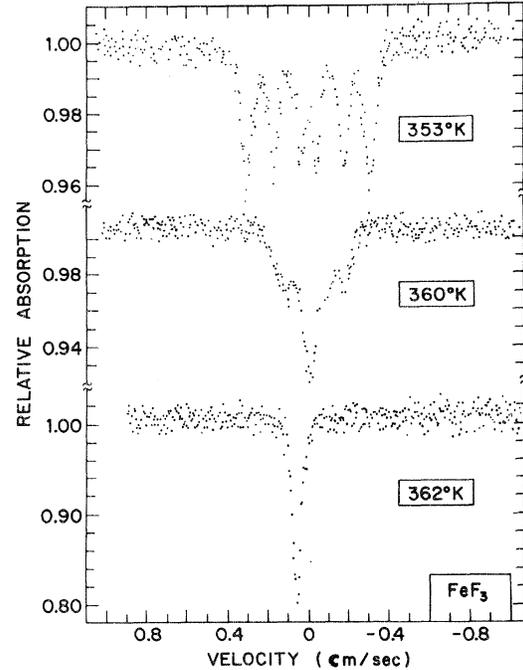
FIG. 2. Some typical spectra of the canted antiferromagnet FeF_3. A powdered absorber was used with effective thickness 3.

The count rate obtained multiplied by 1.04 gives the desired background rate owing to the high-energy γ radiation. A background check was made for each run. The level of 60.5% background was constant throughout the experiment.

(e) *Experimental geometry.* The Mössbauer absorbers were located 60 mm distant from the collimated (1-mm-lead iris) source, and the iris determining the scattering angle was 50 mm distant from the absorber. A general layout of the experimental arrangement is shown in Fig. 1. The iris for the scattering angle was composed of lead disks of radius r and lead washers of inner radius $r + \Delta r$. For the 1° 30' scattering angle, $r + \Delta r = 1.5$ mm. For 3°3', $r = 3.5$ mm, $r + \Delta r = 4.5$ mm, and for 6°, $r = 5.8$ mm and $r + \Delta r = 6.8$ mm (Fig. 1). The transducer, the cryo-oven, the collimators, and the detector were colinearly located on an optical bench.

III. EXPERIMENTAL RESULTS

A typical set of Mössbauer magnetically split spectra is shown in Fig. 2 as a function of temperature for the canted antiferromagnet FeF_3. A spectral anomaly is observed above 355 °K, where a simultaneous presence of both six resolved lines and a central line is observed. The same behavior of the hyperfine splitting was observed by Levinson and co-workers[9] for FeF_3. The spectra were

TABLE I. Fractional intensity of the six-line area relative to the total spectral area in the neighborhood of T_c for FeF_3 spectra shown in Fig. 1.[a]

T °K	293	348.2	357	359	360	361	362
Fractional hfs area (%)	93 ± 1.6	90 ± 1.5	65 ± 1.6	50 ± 0.2	34 ± 0.8	1 ± 0.8	0 ± 0.1

[a]The uncertainty is regarded here as the deviation from the best fit according to the count rate.

analyzed in a way similar to that suggested in Ref. 9. The best fit was obtained for the line width of 0.30 mm/sec, and the intensity ratios of 3 : 2 : 1 : 1 : 2 : 3 for the six Mössbauer transitions. The fractional intensity of the total six-line area relative to the total spectral area close

FIG. 3. (a) The temperature dependence near T_c of the reduced magnetization of FeF_3, $h = H_n(T)/H_n(0)$; $H_n(T)$ is the effective field at the nucleus at a temperature T, obtained by computer fit from the Mössbauer spectra. $H_n(0)$ (=245 kOe) is the field extrapolated to 0 °K from $H_n(T = 4.2$ °K). (b) Scattered intensity (integral count rate for run time of 15 min at each temperature) for various scattering angles.

to T_c is given in Table I. A phenomenological representation of an abnormal spectrum composed of six-line hyperfine splitting and a seventh central line requires the introduction of an effective spin relaxation time of the order of 10^{-9} sec.

The reduced magnetization $h(T)$ was obtained for each sample from the recorded spectra, indicating the approach to the critical temperature T_c, and is shown in Fig. 3(a) for FeF_3 and Fig. 4(a) for Fe_3C. $h(T)$ [as defined in the caption of Fig. 3(a)] is assumed to be proportional to the reduced magnetization[16] and follows a power law with $\beta = \log h / \log(1 - T/T_c) = 0.36 \pm 0.02$ for FeF_3 and 0.34 ± 0.02 for Fe_3C, in the region $0.85 < T/T_c < 0.99$.

The scattered intensity measured by the scaler for periods of 15 min at each temperature (integral count rate) is shown for various angles in Fig. 3(b) for FeF_3, Fig. 4(b) for Fe_3C, and Fig. 4(c) and 4(d) for the nickel iron and pure nickel. The results of the nickel-iron alloy show a multiple scattering (saturation) effect for the small angle, as well as for the large-angle measurements. This is expected for a $t = 10$ absorber.

It is seen from the results that the scattered intensity is angle dependent, and a reduction is noted with the increasing scattering angle. It is also evident from the results that in the absence of Fe^{57} Mössbauer nuclei no increase in the count rate is observed (or is, at least, negligible) suggesting the importance of the presence of the Mössbauer isotope. Experiments were done with a velocity range beyond the spectral range ($|v| > |v_{spect}|$), where no angle-dependent increase in the integral count rate was observed in any of the studied samples, as T approached T_c. In the range $|v| > |v_{spect}|$, the radiation is composed of some background and of 14.4 keV. A fraction of these 14.4-keV γ rays is emitted recoilless by the source, but not resonantly absorbed by the target nuclei. The pure nickel sample does not exhibit any detectable critical behavior of the count rate. These findings suggest that the recoilless process is important, and that only the resonantly absorbed and reemitted 14.4-keV γ rays contribute to the small-angle critical behavior of the count rate.

FIG. 4. (a) Reduced magnetization $h(T)$ for powdered Fe_3C ferromagnet ($t=3$). $H_n(0)$ was extrapolated to 255 kOe. (b) The scattered intensity of Fe_3C at various temperatures for scattering angles of $1°30'$ and $9°$. (c) Small- and large-angle scattering of Ni + 2-at.% Fe_{57} alloy with an effective thickness $t=10$. The increase in the count rate at and above T_c is due to multiple scattering in this thick absorber. (d) Small-angle scattering by a pure-nickel foil of the same atomic thickness and geometry as in (c).

IV. DISCUSSION

A comprehensive analysis of a similar anomaly observed in Mössbauer spectra close to the magnetic critical temperature[7,8] as seen in the example of Fig. 1, was given by Levinson et al.[9]: It is well known that the Mössbauer hyperfine splitting is affected by spin-relaxation processes, particularly in magnetic insulators. A qualitative interpretation[9] suggests collective spin flips of small clusters of aligned magnetic moments in the lattice. In this picture the magnetic clusters are assumed to possess "superparamagnetic" features. It is customary to express the resultant relaxation process by a characteristic relaxation time, τ_F $= \tau_0 \, e^{Kv_{eff}/k_BT}$, where τ_0 is a parametric constant of about 10^{-11} sec. Here K is the effective anisot-

ropy per unit volume and v_{eff} is the volume of a cluster of spins flipping coherently with relaxation time τ_F. Since $\tau_0 \ll \tau_L$ (τ_L being the Larmour nuclear period), the Mössbauer spectrum of the fine v_{eff} regions is exchange narrowed, and a single peak is observed. τ_F is an extremely strong function of Kv_{eff}, and a *small* spread in Kv_{eff} yields the coexistence of hyperfine splitting with a single peak.[9] In this model v_{eff} has a small spread around $\bar{v}_{eff} \sim 10^{-17}$ cm^3 (or of linear dimensions of about 200 Å). When T approaches T_c, $K \rightarrow 0$, thus increasing the spin-flip frequency.

However, the appearance of a pronounced maximum in the small-angle scattering in the neighborhood of T_c suggests that the spatial extent of these $\bar{v}_{eff}$ is temperature dependent. This is apparently a result of spontaneous coherent fluctuations in the magnetic-moment density that increase in magnitude as T_c is approached from below and above and become very large as $T = T_c$. The existence of such fluctuations in the dimensions of the magnetic clusters is supported by neutron-scattering experiments.[4]

The experiments reported in this work relate the relaxation effects observed in Mössbauer spectra to the observed critical behavior of the small-angle scattered intensity.

If the small-angle scattering is due to regions in which the mean internal field averaged over the nuclear lifetime is zero, a rough estimate of the size of such clusters contributing to the critical scattering into an angle θ can be done: $D \simeq \lambda(\text{Å})/\theta(\text{rad}) = 32$ Å for the $1.5°$ iris, ~ 16 Å for the $3.5°$ scattering angle and ~ 9 Å for the $6°$ angle.

The order of 10 Å obtained here is smaller by an order of magnitude from the value of $D \approx 200$ Å suggested by Levinson and co-workers for their superparamagnetic relaxation process. Such large clusters can not contribute to the appreciable scattering into the larger angles ($3.5°$ and $6°$).

The small-angle Mössbauer scattering reveals spatial inhomogeneities of the mean internal field which persists for times of the order of the nuclear lifetime of $\sim 10^{-7}$ sec for Fe^{57} and is responsible for the single peak shown in Fig. 1, or larger life times (six absorption lines). The critical scattering corresponds to *elastic* scattering from these clusters.

The critical scattering of x-rays reveals "instantaneous" fluctuations and that of neutrons fluctuations lasting $\sim 10^{-13}$ sec. These rapid fluctuations exist both above and below T_c, but the mean internal field over a time of the order of 10^{-7} sec vanishes above T_c except in an exceedingly small temperature range around T_c for high- and medium-T_c materials, and thus the absence of critical Mössbauer scattering above the critical temperature.

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