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Observation of a Time-Dependent Recoilless Fraction*†

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We have directly observed a time-dependent recoilless fraction. This effect is seen using delayed-coincidence Mössbauer spectroscopy. The time-dependent recoilless fraction is observed at the Fe^{3+} site and not at the Fe^{2+} site in a $CoSO_4 \cdot 7H_2O$ source. The relaxation time of the recoilless fraction is estimated to be between 10 and 100 nsec. Delayed-coincidence Mössbauer spectroscopy measurements on sources of $CoCl_2 \cdot 6H_2O$ and $Co(NH_4)_2(SO_4)_2 \cdot 6H_2O$ did not show such an effect.

Several authors[1-5] have pointed out the possibility of observing an excited localized mode of vibration using the Mössbauer effect. The general idea is that a relatively energetic nuclear event preceding the Mössbauer transition sets the nucleus vibrating with respect to its equilibrium position in the lattice. This vibrational state will exhibit a mean square nuclear displacement which is not, in general, equal to the thermal-equilibrium value. This "heated localized mode" will eventually relax. The relaxation rate will depend on the rate at which the localized-mode's energy can be transferred into the normal modes. The recoilless fraction depends on the mean square displacement of the radiating nucleus. Therefore, if the lifetime of this vibrational mode is of the same order as the lifetime of the nuclear state, the resulting Mössbauer energy spectrum will reflect the modulation of the exponential decay by this recoilless-fraction relaxation. Thus the spectrum will differ from the one obtained if the vibrational mode decayed very quickly. In the simplest cases, the existence of a time-dependent recoilless fraction would produce a reduction in the Mössbauer effect and in particular a narrowing of the Mössbauer peaks. These effects are not easy to see unambiguously using the regular Mössbauer effect. Indeed, the linewidth and intensity obtained in the absence of a time-dependent recoilless fraction depend on sample thickness, collimation geometry, and nuclear environmental inhomogeneities.

The technique of delayed-coincidence Mössbauer spectroscopy (DCMS) permits the experimentalist to look directly at time-dependent effects. For the case of the Fe^{57} nucleus, the method is as follows. Co^{57} undergoes electron capture to form the second excited state of the Fe^{57} nucleus which decays by the emission of a 122-keV γ ray to the 14.4-keV first excited state. The detection of the 122-keV γ ray signals the formation of the 14.4-keV Mössbauer level. By using this "signal" γ ray in delayed coincidence with the 14.4-keV γ ray, a transmission experiment can be performed corresponding to a preset time interval with respect to the "signal" γ ray; i.e., time $t = 0$. (See Hoy, Hamill, and Wintersteiner[6] for a more complete review of the technique.) The modification of the Mössbauer transmission line shape, due to time selection only, has been calculated classically[7] and quantum mechanically.[8] The results are called "time filtering" and have been experimentally checked quantitatively.[9]

Figure 1 shows the calculated results for a single-line Mössbauer spectrum according to time filtering. The preset time intervals have been chosen to agree with our experimental time windows. In this time-filtering calculation there is only one free parameter, which is the size of the dip. Once this parameter is set for one time

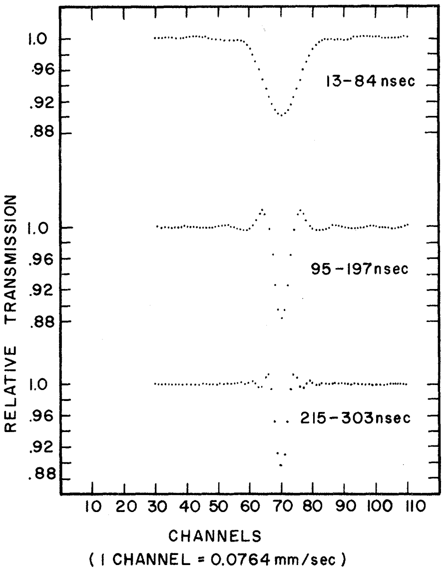

FIG. 1. Calculated single-line Mössbauer transmission spectra according to time-filtering theory for three time windows.

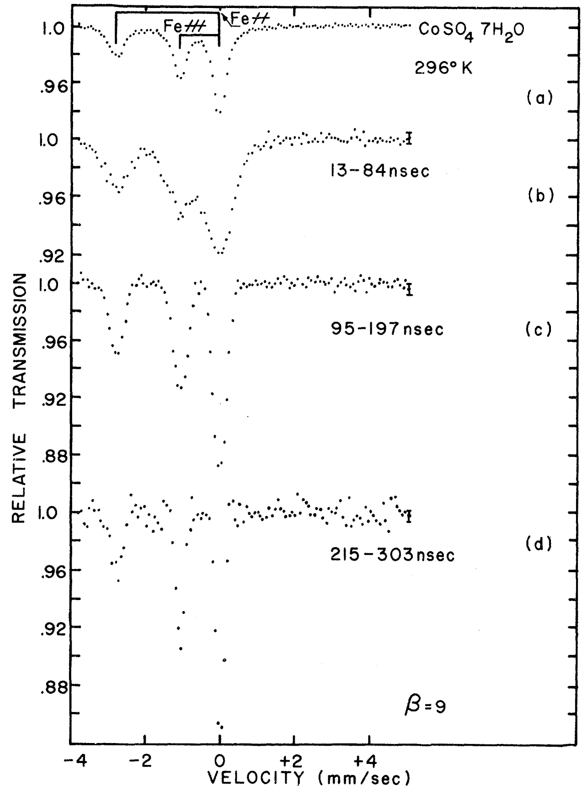

FIG. 2. Experimental results using a $CoSO_4 \cdot 7H_2O$ source at room temperature. (a) The regular Mössbauer effect; (b)–(d) the results using three different time windows.

window, the line shape including the size of the dip for other time windows just follows from the theory. The important feature to observe in Fig. 1, for our present purposes, is that the size of the dip increases and then decreases as the time window moves out in time. Moreover, the *change* in the size of the dip is only 2%. If DCMS experimental data cannot be fitted using these procedures, then time filtering cannot explain the results.

In Fig. 2 we present our experimental results using a $CoSO_4 \cdot 7H_2O$ source.[10] The regular Mössbauer spectrum, Fig. 2(a), shows two charge states, Fe^{2+} and Fe^{3+}, each corresponding to a different quadrupole splitting. Each charge state contributes a symmetric doublet to the Mössbauer spectrum. We can fit this spectrum very well by noting that two dips accidentally fall almost exactly on top of each other. We determine the quadrupole splittings at room temperature to be 2.77 ± 0.01 mm/sec for Fe^{2+} and 1.07 ± 0.01 for Fe^{3+}. The isomer shifts relative to an iron-powder absorber are -1.33 ± 0.01 mm/sec for Fe^{2+} and -0.53 ± 0.01 mm/sec for Fe^{3+}.

This compound has been studied previously[11] using DCMS in order to look for charge-state "after effects." The conclusion was that the Fe^{2+}-to-Fe^{3+} charge-state ratio was not time dependent over the range of times available. These results were analyzed using an empirical approach rather than the full time-filtering theory. Because of this and the known problems of analyzing multilined delayed-coincidence Mössbauer spectra,[12] we decided to re-examine these results. Our experimental results are essentially the same as the earlier ones, but with significantly better statistics. Notice in Figs. 2(b)–2(d) that the left-most dip, which is one peak of the quadrupole doublet from the Fe^{2+} sites, generally follows the time-filtering result in terms of dip size. However, the other two dips show a continuing increase in size as time increases. This result does not follow from time-filtering theory as seen by comparing Fig. 1 with the data. We interpret this result as a time dependence in the recoilless fraction (f) at the Fe^{3+} sites. Notice further that this increase in dip size as a function of time at the Fe^{3+} site cannot be explained by a changing Fe^{2+}-to-Fe^{3+} charge-state ratio due to after effects because it is in exactly the wrong direction. That interpretation would require the Fe^{2+} contribution to grow at the expense of the Fe^{3+} contribution as time increases.

In the regular Mössbauer spectrum of $CoSO_4$

$\cdot 7H_2O$ in Fig. 2(a), observe that the left-most dip is broader than the other two. In the absence of DCMS data, the explanation for the width differences would be difficult to determine. However, given the increase in f as a function of time at the Fe^{3+} sites, the narrower lines corresponding to the Fe^{3+} spectrum are explained by the ideas of Dash and Nussbaum,[4] mentioned above. To put it another way, the increase of f in time weights the longer-lived nuclei more heavily in the regular Mössbauer spectrum than would be the case without this effect. Since, in general in DCMS, longer-lived nuclei give narrower absorption lines than shorter-lived ones (see, e.g., Fig. 1), this bias has the effect of narrowing the Fe^{3+} spectral lines.

There is a fixed number that goes into the time-filtering-theory calculation, which is the absorber thickness conventionally denoted by β. For our case $\beta = 9$. Now if the Dash-Nussbaum approach is valid for the regular Mössbauer effect, it should also apply during the observational time intervals in DCMS experiments. One would expect this effect to show up most clearly in time windows close to time $t=0$, where the time rates of change of the exponential nuclear decay and localized-mode relaxation are most rapid. We do, in fact, see this. When the experimental data shown in Fig. 2(b) are fitted using time-filtering theory, the right two dips are more accurately fitted by using a value of β less than 9. In other words, these two dips seem too narrow. This is again the effect of the time-dependent recoilless fraction modulating the radioactive decay, but now in an early time window.

We have used only three time windows, so it is impossible to give an accurate value for the lifetime of the localized mode. However, making estimates based on Ref. 4, the lifetime is between 10-100 nsec.

We have also done DCMS experiments using other sources; e.g., $CoCl_2 \cdot 6H_2O$ and $Co(NH_4)_2$-$(SO_4)_2 \cdot 6H_2O$. We do not see evidence for a time-dependent recoilless fraction in either of these. For comparison purposes we show our results for $CoCl_2 \cdot 6H_2O$ in Fig. 3. The size of the dips follows ordinary time-filtering theory.

At this time we have no physical explanation why the time-dependent recoilless fraction should appear in $CoSO_4 \cdot 7H_2O$, or why it appears at the Fe^{3+} site preferentially. We are presently investigating the temperature dependence of this effect.

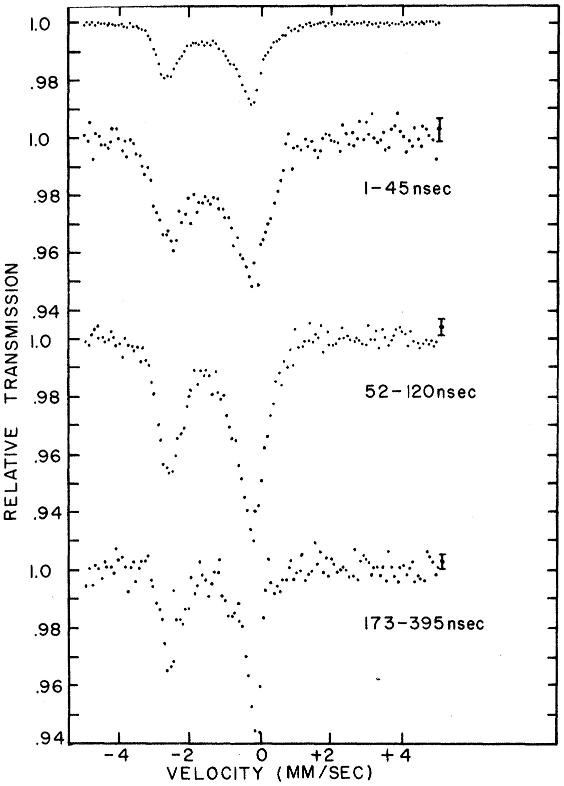

FIG. 3. Experimental results using a $CoCl_2 \cdot 6H_2O$ source at room temperature.

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[†] Portions taken from a dissertation by P. P. Wintersteiner to be submitted in partial fulfillment of the Ph. D. degree.

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