AT-01: MMM–98 Miami, Florida, November 9-12, 1998

Selective Excitation Double Mössbauer Spectroscopy: In Search of Magnetic Relaxation

J. van Lierop and D.H. Ryan

Physics Department, McGill University, 3600 University Street, Montreal, Quebec H3A 2T8, Canada

Abstract

Selective Excitation Double Mössbauer (SEDM) spectroscopy has been used to unambiguously separate the influence of chemical disorder from time-dependent effects in two alloys studied at and above room temperature. a-$Fe_{80}B_{20}$ is a metallic glass with substantial chemical disorder, but no dynamic effects, and the SEDM spectrum can be fitted assuming only disorder broadening. $Fe_{65}Ni_{35}$ is a disordered alloy which may exhibit magnetic relaxation. The SEDM spectra of $Fe_{65}Ni_{35}$ are consistent with chemical disorder, and we rule out magnetic relaxation faster than 2.0±1.2 MHz at 445 K (0.9 T_C).

PACS numbers: 76.80+y, 76.80.Es, 75.50.Kj, 75.50.Bb

Typeset using REVTEX

I. INTRODUCTION

Mössbauer spectra of fine particle systems[1,2] and phase separated alloys[2,3] may show the influences of superparamagnetic relaxation. This time dependent effect on the Mössbauer nucleus causes the hyperfine field to experience a perturbation on the same time scale as the Larmour precession and results in spectral line broadening and energy transitions not available to the nucleus in a stationary hyperfine field. However, many systems which exhibit magnetic relaxation also suffer from chemical disorder, which in turn results in spectral broadening that is similar to that caused by relaxation. Separating these two effects in a conventional transmission Mössbauer spectrum is problematic.

Environment changes during the lifetime of the Mössbauer nuclei can be observed directly by measuring the differential scattering cross section, facilitating the distinction of chemical disorder and magnetic relaxation. This differential scattering cross section is measured using Selective Excitation Double Mössbauer (SEDM) spectroscopy[4–6] by pumping the sample at a fixed energy and Mössbauer analyzing the scattered radiation.

We used a-$Fe_{80}B_{20}$, a metallic glass with substantial disorder, to establish the features of chemical broadening in a SEDM spectrum, and then searched for the additional effects of relaxation in $Fe_{65}Ni_{35}$. $Fe_{65}Ni_{35}$ is a disordered alloy which exhibits significant chemical broadening[7–9] and may undergo magnetic relaxation[3]. Our SEDM spectra of $Fe_{65}Ni_{35}$ are consistent with a previous room temperature SEDM spectrum of an Fe-Ni Invar alloy[10] and support descriptions of Fe-Ni Invar alloy transmission lineshapes in terms of static, inhomogeneous hyperfine field distributions[7,9]. Using the signature of magnetic relaxation in SEDM spectra, we determine a new upper limit for the supermoment fluctuation rate possible in $Fe_{65}Ni_{35}$.

II. EXPERIMENTAL METHODS

The alloys were prepared by arc-melting the appropriate ratio of pure elements under Ti-gettered argon and then melt spun under a partial pressure of helium onto a stainless steel wheel at 30 m/s for $Fe_{65}Ni_{35}$ and onto a copper wheel at 50 m/s for a-$Fe_{80}B_{20}$. Absence of crystallinity in a-$Fe_{80}B_{20}$ was confirmed using Cu K_α x-ray diffraction. X-ray diffraction spectra of $Fe_{65}Ni_{35}$ displayed the expected crystalline peaks. Thermogravimetric analysis determined a Curie temperature of 496 K[11] for $Fe_{65}Ni_{35}$ and a Curie temperature of 658 K for a-$Fe_{80}B_{20}$. Some $Fe_{65}Ni_{35}$ ribbon was annealed at 800 K for an hour and the expected five degree increase in the Curie temperature was observed[8].

Transmission Mössbauer measurements were done with a constant acceleration spectrometer using a 1 GBq ^{57}Co**Rh** source. SEDM measurements used a constant acceleration spectrometer for energy detection and a constant velocity spectrometer for energy selection[6]. Energy calibration was achieved using an α-Fe foil. Samples were mounted in an evacuated furnace for spectra at temperatures up to 500 K.

Transmission spectra of a-$Fe_{80}B_{20}$ and $Fe_{65}Ni_{35}$ were fitted using Window's method[12]. The distribution of hyperfine fields, $P(B_{hf})$ and relative intensities of the spectral lines from the transmission fits were then used to parameterize SEDM spectra. Fitting parameters for SEDM spectra were restricted to the baseline counts, linewidth and intensity, *i.e.* all critical Mössbauer parameters were determined from the transmission spectra. The transmission spectra were also used to determine the location of line #1 for the constant energy drive when measuring the SEDM spectrum.

The broadening in the transmission spectra of $Fe_{65}Ni_{35}$ may also be described using the stochastic two state (spin-flip) magnetic relaxation model of Blume and Tjon[13]. Following the fitting procedures described by Rancourt *et al.*[3] for $Fe_{65}Ni_{35}$, we have analyzed our transmission spectra assuming a single hyperfine field. Field and linewidth were determined from room temperature spectra and kept fixed for all other temperatures. Magnetic relaxation was characterized by the supermoment fluctuation rate and average magnetization.

Fluctuation rates from these fits should, in principle, also describe the SEDM spectrum of the same temperature. However, only partial solutions to the problem of measuring the differential scattering cross section of Mössbauer nuclei in a time dependent environment exist.

A simple model due to Balko and Hoy[6] is valid in the limit of slow relaxation, dealing only with line broadening, applicable to SEDM spectra where lines due to the energy transitions $m_I{=}\pm\frac{1}{2}$, $m_I{=}\pm\frac{3}{2}$ are visible. A more comprehensive description for paramagnetic systems was developed by Balko[14], however we have been unable to reconstruct this method. For the interim, until a comprehensive formalism for SEDM measurements on time dependent systems is established, we offer a simpler model. The formalism used for transmission lineshapes models the Mössbauer nucleus as oscillating between two states by flipping the direction of the hyperfine field by 180°, so for example, an excited nucleus alternates between a $m_I{=}-\frac{3}{2}$ state and a $m_I{=}+\frac{3}{2}$ state at the relaxation frequency while it decays into the ground state. We calculate the intensities of lines correlated by magnetic relaxation by breaking up the exponential decay of Mössbauer nuclei into pieces the size of the relaxation time. Normalizing these expressions and using a Markov process argument, the relative line intensities due to dynamic effects during a SEDM experiment are obtained. The results of this model are consistent with those of Afanas'ev and Sedov[15].

Taking the relaxation rates determined from fits to the transmission spectra and combining them with our simple model, we can predict the corresponding SEDM spectra. With $< \mathrm{B_{hf}} >$ and isomer shift from the field distribution fits of the $Fe_{65}Ni_{35}$ SEDM spectra, we establish an upper bound for magnetic relaxation.

III. RESULTS AND DISCUSSION

Figure 1 presents the transmission Mössbauer and SEDM spectra of a-$Fe_{80}B_{20}$ at room temperature (0.45 $\mathrm{T_c}$). The transmission spectrum exhibits the usual broadened six-line pattern of a metallic glass with a broad hyperfine field distribution, $\mathrm{P(B_{hf})}$. SEDM data obtained driving line #1 show a single broad line which may be fitted assuming the same $P(B_{hf})$ determined from the transmission spectrum. This is direct evidence that chemical disorder can be detected using SEDM spectroscopy.

$Fe_{65}Ni_{35}$ presented similar broadened six-line spectra with varying temperature. Static fits of the transmission spectra for $Fe_{65}Ni_{35}$ at various temperatures yielded hyperfine field distributions similar to those reported previously[9]. As with a-$Fe_{80}B_{20}$, SEDM spectra obtained while driving line #1 of $Fe_{65}Ni_{35}$ show only a single broadened line at all temperatures examined. This result is immediately inconsistent with significant relaxation rates. Indeed, fitting the SEDM spectra assuming the static distribution of hyperfine fields derived from the corresponding transmission spectrum yields a complete description of the data with no other variable parameters (Fig. 2).

Using the relaxation model to fit the transmission spectra of $Fe_{65}Ni_{35}$ also yields adequate fits, and a plot of the logarithm of the supermoment fluctuation rate versus the reciprocal of temperature is shown in Figure 3. Using the rate from the transmission analysis, we can calculate the expected SEDM pattern using the model described above. With the large fluctuation rates at high temperature, a strong peak from the m_I=$+\frac{3}{2}$, m_I=$+\frac{1}{2}$ transition should be present, However the 445 K spectrum shown at the bottom of Figure 2 clearly demonstrates that the relaxation rate derived from the transmission fit is far too high. Fluctuation rates derived from SEDM spectra using our simple model for some of the temperatures investigated are included in Figure 3 and lie almost two orders of magnitude below those derived by assuming that all of the observed spectral broadening in the transmission spectra is due to relaxation effects. If relaxation effects are present, they cannot be happening at rates any faster than 2.0±1.2 MHz at 445 K (0.9 T_C).

IV. CONCLUSIONS

SEDM has been used to distinguish static and dynamic contributions to the spectral broadening observed in conventional transmission Mössbauer spectra.

Measurements on a-$Fe_{80}B_{20}$ provide a clear example of the effects of static, chemical disorder on transmission and SEDM spectra. A inhomogeneous distribution of hyperfine fields yields an accurate description of both a-$Fe_{80}B_{20}$ transmission and SEDM spectra and the influence of chemical broadening can be easily detected with SEDM spectroscopy, and is fully consistent with transmission data.

Comparison of static and dynamic fits to both transmission and SEDM spectra of $Fe_{65}Ni_{35}$ at temperatures up to 0.9 T_c allow us to rule out relaxation as a significant source of broadening in this system. All of the observed line broadening in $Fe_{65}Ni_{35}$ arises from chemical disorder. Any time dependent effects which may be present are slower than 2 MHz and make a negligible contribution to the spectral form. This description is fully consistent with previous interpretations of Fe-Ni Invar transmission spectra in terms of chemical disorder alone[7,9].

SEDM spectra of $Fe_{65}Ni_{35}$ provide conclusive evidence that chemical disorder is responsible for the lineshapes of transmission spectra on Fe-Ni Invar alloys.

This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada and Fonds pour la formation de chercheurs et l'aide à la recherche, Québec. We would like to thank N. de Takacsy for helpful discussions relating to relaxation theory.

V. FIGURE CAPTIONS

Figure 1 Transmission Mössbauer spectra of a-$Fe_{80}B_{20}$ (top), a metallic glass, at room temperature and SEDM spectra of same examining line #1 (bottom).

Figure 2 Transmission Mössbauer spectra of $Fe_{65}Ni_{35}$ (top) obtained at indicated temperatures fit using a distribution of hyperfine fields and SEDM spectra of line #1 (bottom). Similar results were obtained by Price and Stewart[10] on $Fe_{66}Ni_{34}$ at 295 K.

Figure 3 Logarithm of the supermoment fluctuation rate as a function of reciprocal temperature from transmission Mössbauer spectra fits. Values from Rancourt *et al.*[3] for comparison. Room temperature spectra fit had poor convergence, similar to Rancourt *et al.*, so frequency for that temperature is approximate. Estimates of the fluctuation rates from SEDM data are plotted, displaying discrepancy with transmission fit results.

REFERENCES

[1] J.L. Dormann, D. Fiorani and E. Tronc, in "*Advances in Chemical Physics*", **XCVIII**, eds. I. Prigogine and Stuart A. Rice (John Wiley & Sons, Inc.), 283 (1997).

[2] L. Cianchi, P. Moretti, M. Mancini and G. Spine, Rep. Prog. Phys. **49**, 1243 (1986).

[3] D.G. Rancourt, H.H.A. Smit and R.C. Thiel, J. Magn. Magn. Mater. **66**, 121 (1987).

[4] A.N. Artem'ev, G.V. Smirnov and E.P. Stepanov, Soviet Physics JEPT **27**, 547 (1968).

[5] Neil D. Heiman and J.C. Walker, Phys. Rev. **184**, 281 (1969).

[6] Bohdan Balko and Gilbert R. Hoy, Phys. Rev. B **10**, 36 (1974).

[7] Jürgen Hesse and Eckhard Hagen, Hyperfine Interact. **28**, 475 (1986).

[8] M.R. Gallas and J. A. H. da Jornada, J. Phys.: Condens. Matter **3**, 155 (1991).

[9] H.R. Rechenberg, Hyperfine Interact. **54**, 683 (1990).

[10] D.C. Price and A.M. Stewart, Hyperfine Interact. **42**, 1157 (1988).

[11] E.F. Wassermann, in "*Ferromagnetic Materials*", **V**, eds. K.H.J. Buschow and E.P. Wohlfarth (North-Holland, Amsterdam), 240 (1990).

[12] B. Window, J. Phys. E **4**, 401 (1971).

[13] M. Blume and J.A. Tjon, Phys. Rev. **165**, 446 (1968).

[14] Bohdan Balko, Phys. Rev. B **33**, 7421 (1986).

[15] A.M. Afanas'ev and V.E. Sedov, Hyperfine Interact. **56**, 1425 (1990).

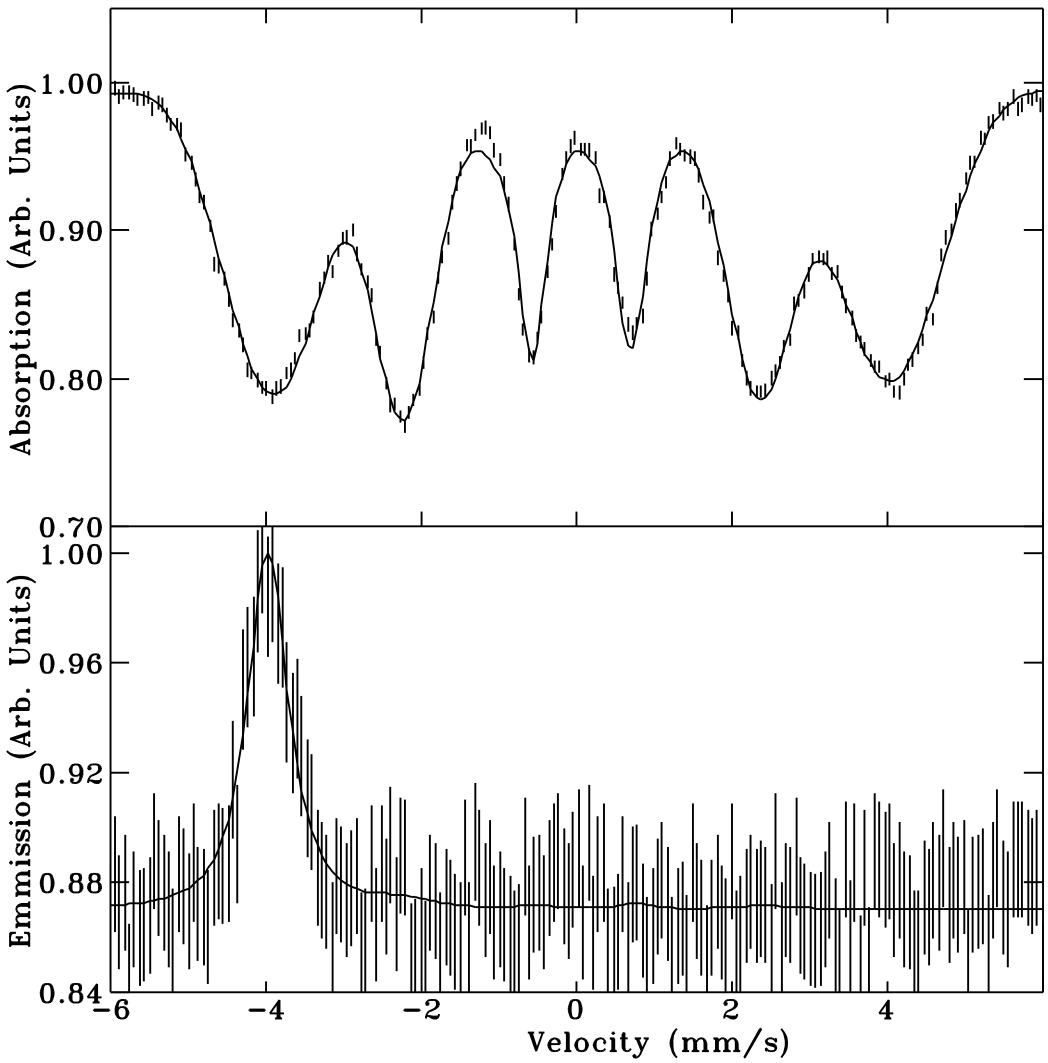

FIG. 1. van Lierop, AT-01: MMM-98 Miami, Florida Nov 9–12 1998 (J. Appl. Phys.)

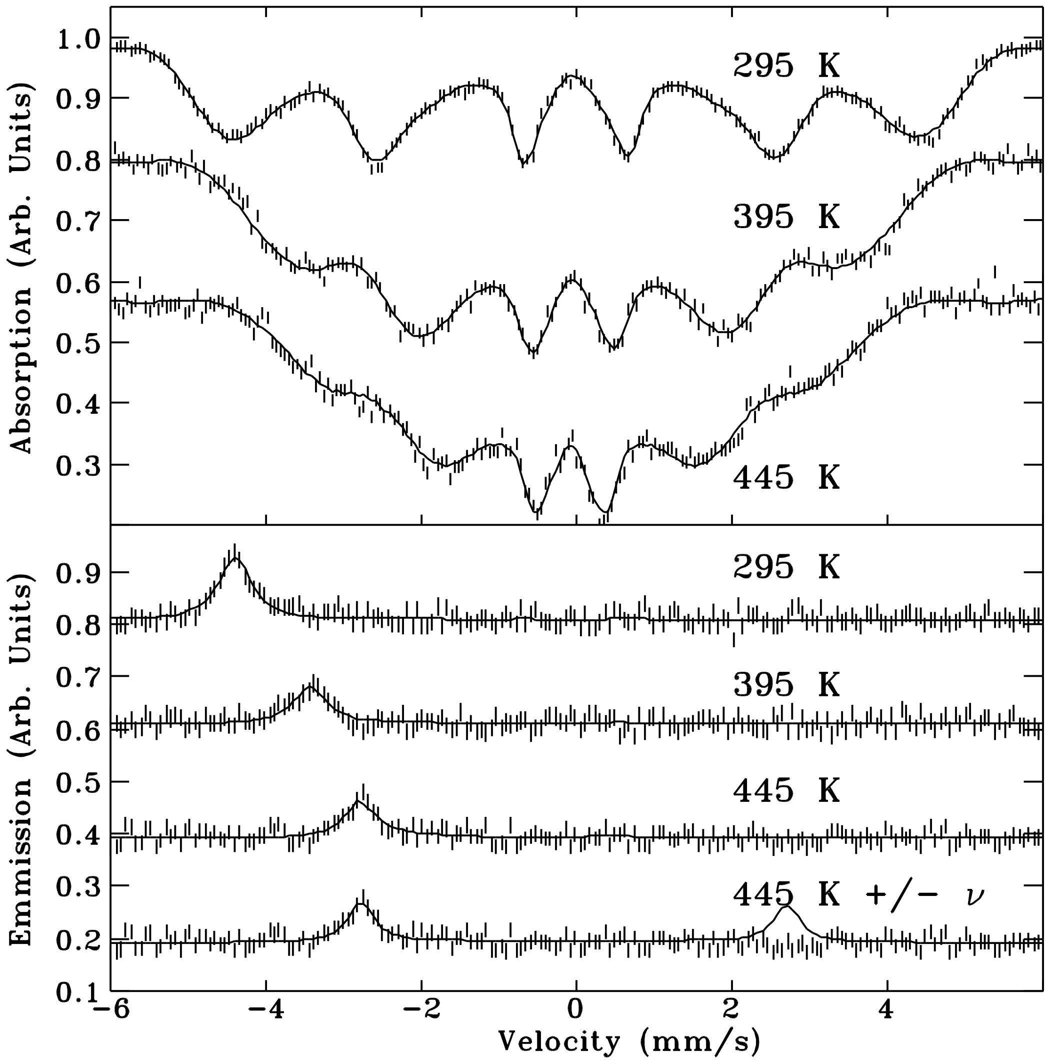

FIG. 2. van Lierop, AT-01: MMM-98 Miami, Florida Nov 9–12 1998 (J. Appl. Phys.)

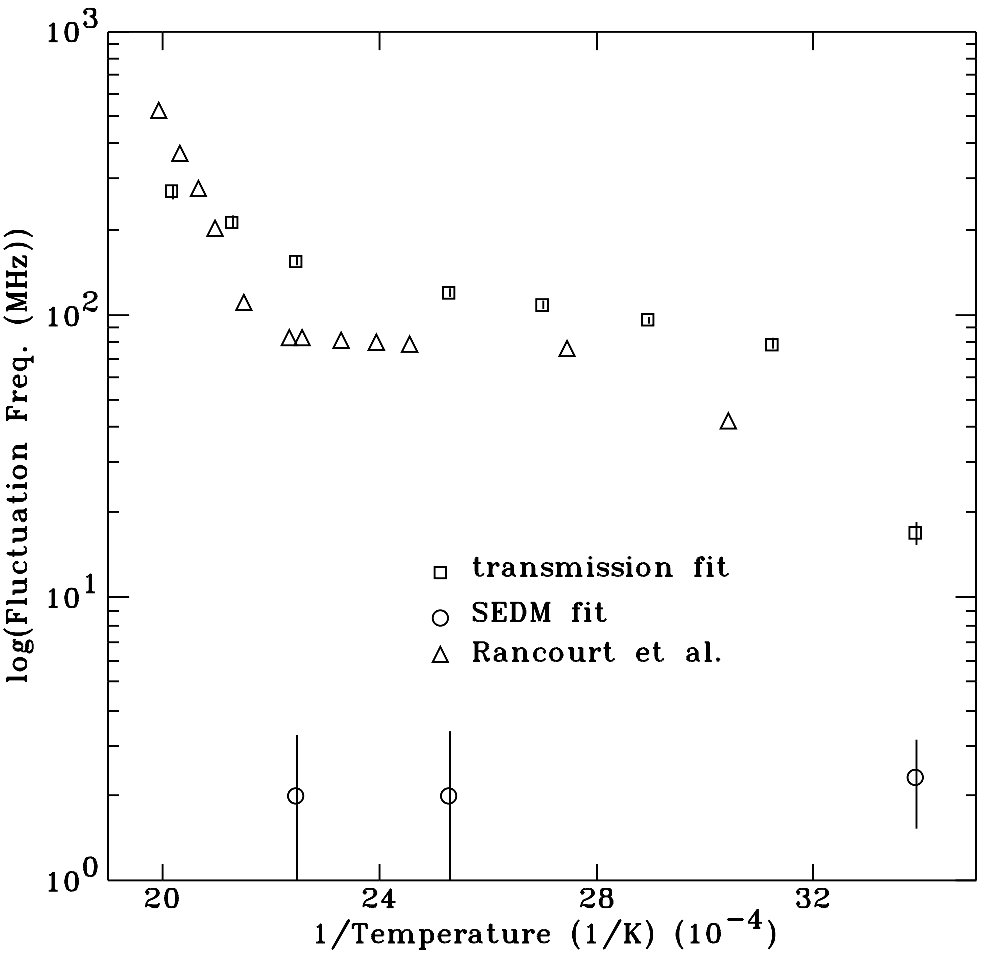

FIG. 3. van Lierop, AT-01: MMM-98 Miami, Florida Nov 9–12 1998 (J. Appl. Phys.)