Spin-relaxation model for the Mössbauer spectra of $BaSn_xTi_{2-x}Fe_4O_{11}$: A ferric oxide spin glass

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A spin-relaxation model was used to interpret the ^{57}Fe Mössbauer spectra of the ferric oxide spin glass $BaSn_xTi_{2-x}Fe_4O_{11}$, with $x = 0.0, 0.4, 0.8, 1.2, 1.6$, and 2.0. This interpretation is suggested as an alternative to distributions of static hyperfine nuclear fields, which require many free parameters to account for the temperature dependence of the spectra, and do not have an obvious physical interpretation. The spin-relaxation analysis used here reduces to the number of free parameters to essentially two: a spin-freezing molecular field and an electronic spin-flip frequency. The results verify the existence of a double magnetic transition in the sample with $x = 0.0$, and the suppression of the upper transition in the samples with $x = 0.4$ and 0.8. The results also suggest the presence of a double magnetic transition in the samples with $x > 1.0$ which has not been observed using other measurements, and may be related to a known difference in structure between the $x = 0.0$ and 2.0 samples. The least-squares fits obtained rival the results of distributions of static fields while requiring fewer free parameters that have direct physical significance. It is suggested that many analyses of spin-glass materials in terms of static-hyperfine-field distributions should be reconsidered.

I. INTRODUCTION

The Mössbauer effect has been used extensively to study the low-temperature magnetic properties of spin glasses. A major problem with the interpretation of the spectra obtained is the broadness of the spectra, especially near the glass transition. This broadness is observed in many spin-glass systems of different compositions, and seems to be characteristic of these types of systems. The main method of analyzing the spectra has been in terms of distribution of static-hyperfine nuclear fields, arising presumably due to differences in magnetic ordering at different sites and the random environments in the disordered system. Many examples of this type of analysis can be found in the literature (see, for example, Refs. 1, 2, and 3). A clear physical interpretation of the broad hyperfine-field distributions in spin glasses has been elusive. An alternative to this interpretation of the broad spectra line shapes in terms of spin-relaxation and stochastic models is suggested in this work.

Hyperfine-field distributions are found in iron alloys, for example, where it is found that the hyperfine field at an iron nucleus at a given site is dependent on the occupancy of the nearest-neighbor shell, thus random alloys often show very broad spectra with overlapping lines due to various types of iron environments (this makes the Mössbauer effects a useful tool to study microscopic structure in such alloys). Therefore, most spectral analyses of the dilute magnetic alloy spin glasses have been in terms of static-hyperfine-field distributions (despite difficulty in interpretation), and this may account for the widespread use of this method. In ferric oxides, however, the hyperfine field is mainly a property of the ion itself and not very sensitive to the environment of the ion. For example, dilution of the iron in α-Fe_2O_3 with 23 at. % Al creates virtually no line broadening at all, despite the extreme randomness of the system, just a slight decrease in

the hyperfine splitting due to a drop in the Néel temperature.[4] Nonetheless, typical broad spectral line shapes are observed in ferric oxide spin glasses, and the origin of hyperfine-field distributions in these materials is thus particularly difficult to understand.

An assumption which is made in using distributions of static fields is that the spin-relaxation rates and hence hyperfine-field fluctuations are occurring over time scales much shorter than the Larmor precession time of the nuclear moment, so that the nucleus "sees" only a time-average hyperfine field which can be considered static. However, as shown in Ref. 5, the spin-relaxation rates in some spin-glass materials, as measured by muon spin resonance and neutron spin echo techniques, decrease by orders of magnitude as the temperature is lowered below the glass temperature, and can be on the order of the Larmor frequencies of the nuclear moments (about 10–100 MHz for ^{57}Fe in typical systems). Since the hyperfine nuclear spin is due to the atomic moment, this suggests that an interpretation in terms of static hyperfine fields is not warranted. This is not to say that hyperfine-field distributions do not exist in some spin glasses (e.g., Fe alloys), but rather that dynamical effects account for the anomalous broadening. It might be noted that the broad "smearing" suggested by these distributions of hyperfine fields has often been used as evidence for the lack of a sharp transition in these materials, with different moments ordering at different temperatures. It is suggested here that these broad distributions are artifacts of fitting procedures which ignore hyperfine-field fluctuations, and a dynamical model is necessary to interpret the spectra. In this work a spin-relaxation model is applied to the Mössbauer spectra of the ferric oxide system $BaSn_xTi_{2-x}Fe_4O_{11}$, which shows spin-glass properties and the broad spectral line shapes typical of these types of materials. A ferric oxide was chosen specifically for this study, since the hyperfine fields are generally not

affected by the local environments of the iron atoms, and this simplifies the analysis of the spectra. The analysis is generally applicable to other Fe^{3+} oxide spin glasses, which have similar spectral line shapes.

II. STOCHASTIC RELAXATION THEORY

The stochastic line-shape theory of Anderson[6] and Sack[7] has been applied to a wide variety of phenomena, such as motional narrowing in NMR and pressure broadening in sodium street lamps, and has also been applied to Mössbauer spectroscopy.[8,9] The model used here is due to Dekker,[8] and models the ferric ion as a spin 5/2 subjected to a molecular field and undergoing transitions between the six atomic spin states along the quantized axis. This model is intended to give the Mössbauer line shape in situations where spin fluctuations are occurring over time scales comparable to the Larmor precession time of the nuclear moment. The model contains essentially two free parameters: a local molecular field which creates a preferred direction for the ionic moment and Boltzmann weights the various spin states, and an electronic spin-flip frequency which may be on the order of the Larmor frequency of the nuclear moment. The hyperfine field is assumed to be primarily due to the Fermi-contact contribution, which typically has a value of 200–400 kG (per spin) for ferric oxide materials, and is not very sensitive to the environment of the ferric ion.[10] The value of the hyperfine-field magnitude is determined by analyzing the lowest temperature spectrum, for which clear sextet patterns are observed. All hyperfine nuclear parameters (both magnetic and electric) are fixed for all temperatures. This was found to be a reasonable approximation for the $BaSn_xTi_{2-x}Fe_4O_{11}$ system and was done mainly for convenience and reducing the number of free parameters. Thus the broad character of the spectral line shapes is assumed to be due entirely to the two relaxation parameters. The molecular field parameter h can be written

$$h = g\mu_g H_{mol}/k_B T , \qquad (1)$$

where g is the Landé factor, μ_B is the Bohr magneton, and H_{mol} is the molecular field. The derivation of the spectral line shape here parallels Jones and Srivastava,[11] who give a general derivation for any number of spin states. On the assumption that the forces which cause the relaxation can be modeled by a random field perpendicular to the molecular field which causes the atomic spin to perform a random walk between adjacent spin states, the Boltzman independent transition rates between the kth and $(k \pm 1)$th spin states can be written

$$r_{k,k\pm1} = r(S_z, S_z \pm 1) = R[S(S+1) - S_z(S_z+1)] , \qquad (2)$$

where R is the electronic spin-flip frequency. A general expression for the line shape of a given transition given by Sack[7] can be written

$$I(\omega) = 2 \operatorname{Re}[\mathbf{W}\underline{M}^{-1}\mathbf{1}] , \qquad (3)$$

where the matrix $\underline{M}$ is a tridiagonal matrix, the vector $\mathbf{W}$ contains the Boltzmann weights for the spin states, and $\mathbf{1}$

is the unit column. The elements of $\underline{M}$ on the main diagonal can be written

$$M_{kk} = i(\omega - \omega_0 - \delta_k) + \Gamma - M_{k,k+1} - M_{k+1,k} , \qquad (4)$$

where ω_0 is the line position with no magnetic shift, δ_k is the shift due to the hyperfine magnetic interaction when in the kth spin state, and Γ is the linewidth. The off-diagonal elements contain the transition rates, which are assumed to have the values given by Eq. (2) for transitions to lower energy in the molecular field, and are Boltzmann weighted for transitions to higher energy in the molecular field:

$$M_{k,k+1} = -r_{k,k\pm1} , \qquad (5)$$

$$M_{k+1,k} = -r_{k,k\pm1}e^{-h} . \qquad (6)$$

For a spin 5/2 the matrix $\underline{M}$ is six by six. The calculation thus involves the inversion of a six by six matrix, which is easy enough to perform analytically by defining $\underline{M}\mathbf{V}=1$, and solving the simultaneous equations for the vector $\mathbf{V}$. Expression like Eqs. (3) must be summed for each of the six transitions in the Mössbauer spectrum.

Figure 1 illustrates some six-state relaxation line shapes for a wide range of the relaxation parameters. The relaxation rate R is in mm/s (the same units as the abscissa) and values can be obtained in Hz by multiplying by 1.8496×10^6 (Hz sec/mm). The velocity scale ranges from -15 to 15 mm/s, and the hyperfine-field magnitude is held fixed at 220 kG per spin, typical of ferric oxides.
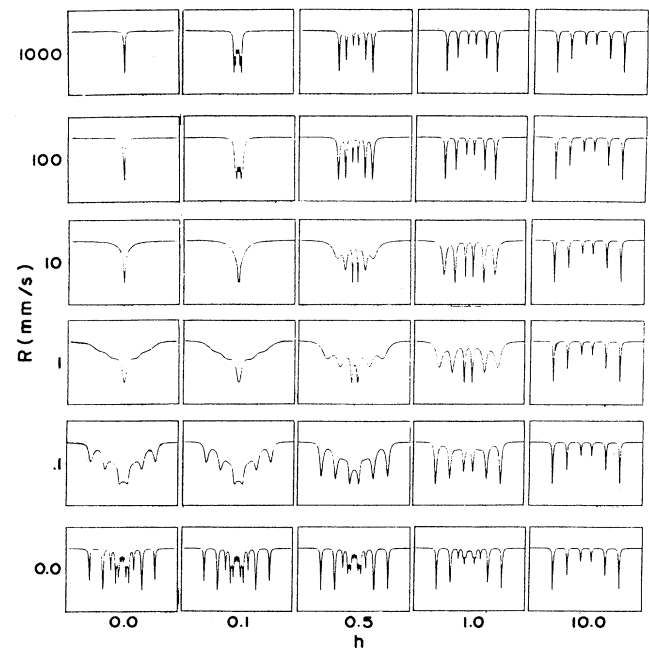

FIG. 1. Six-state relaxation line shapes for various values of h and R. The units of R are in mm/s, the same as the velocity scale, which ranges from -15 to 15 mm/s. The hyperfine-field magnitude is held constant at 200 kG per spin, and all electric hyperfine effects are neglected. The linewidth is 0.3 mm/s.

Electric hyperfine effects are neglected, and the linewidth is fixed at 0.3 mm/s. Note that for large relaxation rates the spectrum consists of sharp sextets with narrow linewidths, with splittings which depend on the molecular field parameter like a Brillouin function. This is the regime in which effective static fields can be assumed. For small relaxation rates, the spectrum consists of superpositions of sextets from the various spin states, giving splittings corresponding to 550, 330, and 110 kg. This can be seen from Eq. (4) by noting that when the off-diagonal elements are zero, the matrix inversion results in a superposition of Lorentzians. The intermediate spin states are Boltzmann weighted by the molecular field, so that in a strong enough molecular field the spin is in the 5/2 state, and a sextet with splittings corresponding to 550 kG results. For relaxation rates on the order of the Larmor frequencies (about 1–10 mm/s, depending on the transition and the atomic spin state) broad spectral line shapes occur, and it is suggested that this behavior is exhibited by spin glasses. The spin-glass transition can thus be characterized by a slowing of the spin-relaxation rate (as illustrated by μSR results), and the onset of a local "spin-freezing" molecular field.

Two quantities which can be calculated from the relaxation parameters are the order parameter q, which is defined here as the (normalized) thermal expectation value of S_z and is given by a Brillouin function of h,

$$q = \langle S_z \rangle / S = B_{5/2}(h) \tag{7}$$

and the spin correlation time, which in the Dekker model can be written

$$\tau_c = [7R(1+e^{-h})]^{-1} , \tag{8}$$

and corresponds to the inverse of the mean relaxation rate between spin states. The spin correlation time calculated this way can be compared with the μSR results of Ref. 5.

In order to account for the quadrupole shifts (which are often neglected completely when using distributions of static-hyperfine fields), a simple model was devised to account for the resulting inhomogeneous broadening in the low-temperature random spin structure. For small shifts, the sign of the shift essentially depends on whether the hyperfine field is parallel or perpendicular to the principal axis of the electric field gradient, and the shift is zero if the angle between them is $\cos^{-1}(1/\sqrt{3})$.[12] So it was assumed that in the low-temperature spectra superpositions of line shapes having positive, negative, and zero shifts would model the inhomogeneous broadening, with magnitudes equal to RMS values of the shifts seen just above the transitions. This effect of quadrupole shifts averaging out and creating line broadening due to many spin directions has been observed in garnets.[13]

III. ANALYSIS OF SPECTRAL DATA

The samples of $BaSn_xTi_{2-x}Fe_4O_{11}$, studied in this work have been studied extensively using magnetic measurements,[14] high resolution transmission electron microscopy,[15] and some Mössbauer measurements.[14,16] Details of the preparation of the samples used in this study
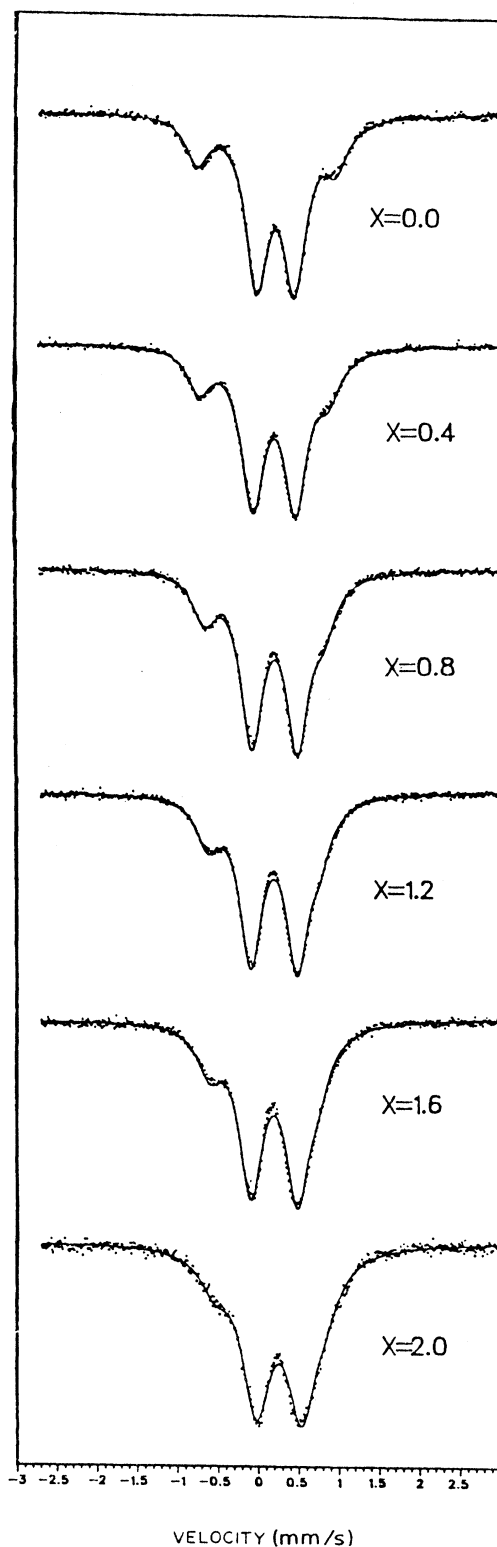

FIG. 2. Room temperature spectra for $BaSn_xTi_{2-x}Fe_4O_{11}$. The more intense doublet in each spectrum arises from the octahedral sites in the crystal.

can be found in Ref. 14. The $BaTi_2Fe_4O_{11}$ crystal has the hexagonal $P6_3/mmc$ structure, and Fe^{3+} ions occupy three crystallographic sites: randomly with Ti^{4+} on (distorted) octahedral $(6g)$ and $(4e)$ sites, and orderly on rather widely separately fivefold $(2d)$ sites (bipyramidal).[15] The $BaSn_2Fe_4O_{11}$ crystal has a slightly different (orthorhombic $Cmcm$) structure with a unit cell twice as large and somewhat different cation arrangement.[15] The room temperature spectra for the $BaSn_xTi_{2-x}Fe_4O_{11}$ system are shown in Fig. 2. The octahedral sites give rise to the more intense doublet and all spectra are fit assuming a superposition of two doublets. The more distorted five fold sites give a correspondingly larger quadrupole splitting than the (nearly) octahedral sites. Note that there is little composition dependence to the spectra, except for a broadening in the Sn-rich compounds which is probably due to the known crystallographic differences between the Ti and Sn compounds, and it has been suggested[16] that the spectra for $BaSn_2Fe_4O_{11}$ are better interpreted in terms of the three doublets rather than two. Intensity ratios between the fivefold and the octahedral sites were found to be in good agreement with the theoretical value of 4/15 for all compositions. It was found that there was little composition variation of the electric hyperfine parameters at temperatures just above the magnetic transitions, and reasonable values were fixed for low-temperature analysis for all samples, to incorporate the effect of quadrupole shifts to first order. The fivefold site was assigned an isomer sift of 0.337 mm/s and a quadrupole shift of 0.683 mm/s, and the octahedral site was assigned an isomer shift of 0.417 mm/s and a quadrupole shift of 0.281 mm/s, and these values were fixed for subsequent spectral analysis at cryogenic temperatures.

The magnitudes of the hyperfine fields for the octahedral and fivefold sites were determined by analyzing the lowest temperature spectra (20 K) of $BaTi_2Fe_4O_{11}$ and allowing the field values to be free parameters. The intensity ratios were held fixed at the theoretical ratios of 4/15, and no attempt was made to distinguish between the hyperfine fields on the two octahedral sites. The results of the least-squares analysis gave a value of 198 ± 5 kG (per spin) on the octahedral sites and 177 ± 20 kG (per spin) on the fivefold sites. The larger hyperfine field and smaller quadrupole shift on the octahedral sites is typical of ferric ions,[17] including Fe^{3+} in garnets,[18] and the value determined is in good agreement with the results of other workers at 4.2 K. All hyperfine structure parameters were held fixed for all compositions and temperatures, and the temperature variation was assumed to be due entirely to the relaxation parameters. It was assumed that the relaxation parameters on the different crystallographic site were the same. This was done mainly in the spirit of minimizing the number of free parameters, although the low relative intensity of the fivefold site may make the determination of differences difficult, at least with the present data. The fitting routines used are after Bevington,[19] and utilize the gradient-expansion algorithm of Marquardt,[20] which combine the best features of a gradient search and linear expansion of the fitting function near the minimum in χ^2.
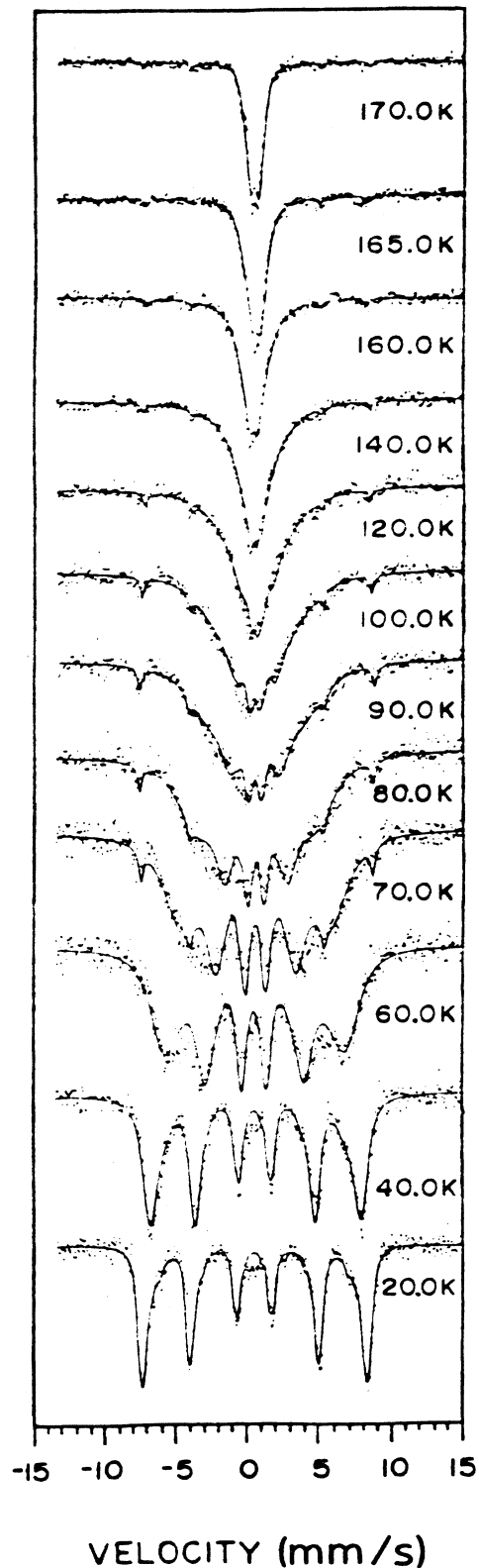

FIG. 3. Mössbauer spectra and least-squares fits for $BaTi_2Fe_4O_{11}$ ($x = 0.0$).

Mössbauer spectra were obtained at temperatures of 20 K and above. Figure 3 shows the spectra and least-squares fits for the $x = 0.0$ sample. Some of the spectra have weak lines visible from a ferrimagnetic impurity (probably based on α-Fe_2O_3, but of unknown composition), and a two-parameter sextet spectrum was superimposed to account for it in the broad spectra. The $x = 0.0$ sample has been shown to have a ferrimagnetic transition at 165 K and a spin-glass transition at 70 K, although the nature of the upper transition is unclear.[14] The order parameter q and spin correlation time τ_c for $x = 0.0$ are shown in Fig. 4. Note that the upper transition is seen by the onset of a nonzero order parameter q and a large slowing of the spin correlation time which saturates in the ferromagnetic phase as the temperature is lowered. The lower transition is seen as a "kink" in q and τ_c, with an approximately power law dependence of τ_c with T in the glass phase. It was found that the upper transition is suppressed as Sn is added to the system, so that only the spin-glass transition is observed. Figure 5 shows the spectra and least-squares fits for the sample with $x = 0.8$, and Fig. 6 shows the order parameter q and spin correlation time τ_c for this sample. Note that the results for this sample are consistent with a sharp transition occurring at

about 80 K (although we are not claiming that the present results confirm such a viewpoint). The sample with $x = 0.4$ was found to be similar, with a single glass transition temperature which is lowered as Sn is added to the system, in agreement with previous findings.[14]
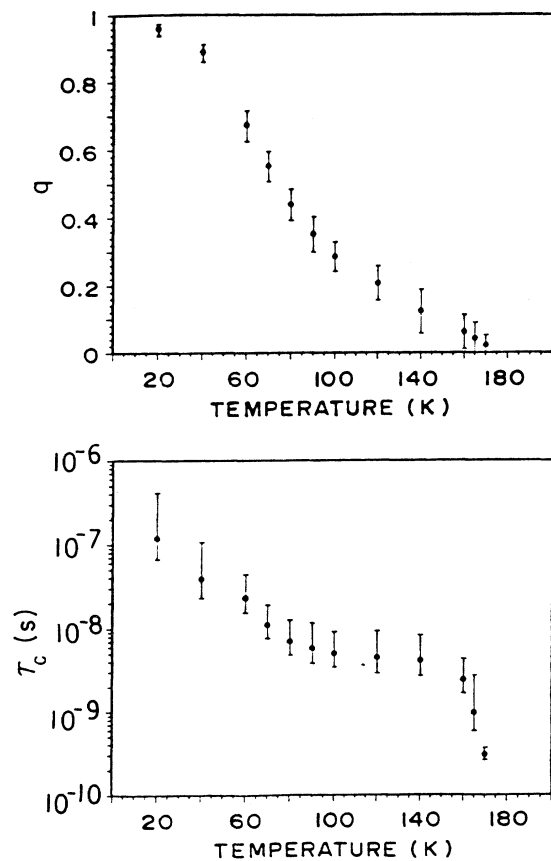

FIG. 4. Order parameter q and spin correlation time τ_c for $x = 0.0$. Note the kink in both quantities at about 75 K, indicating the spin-glass transition.
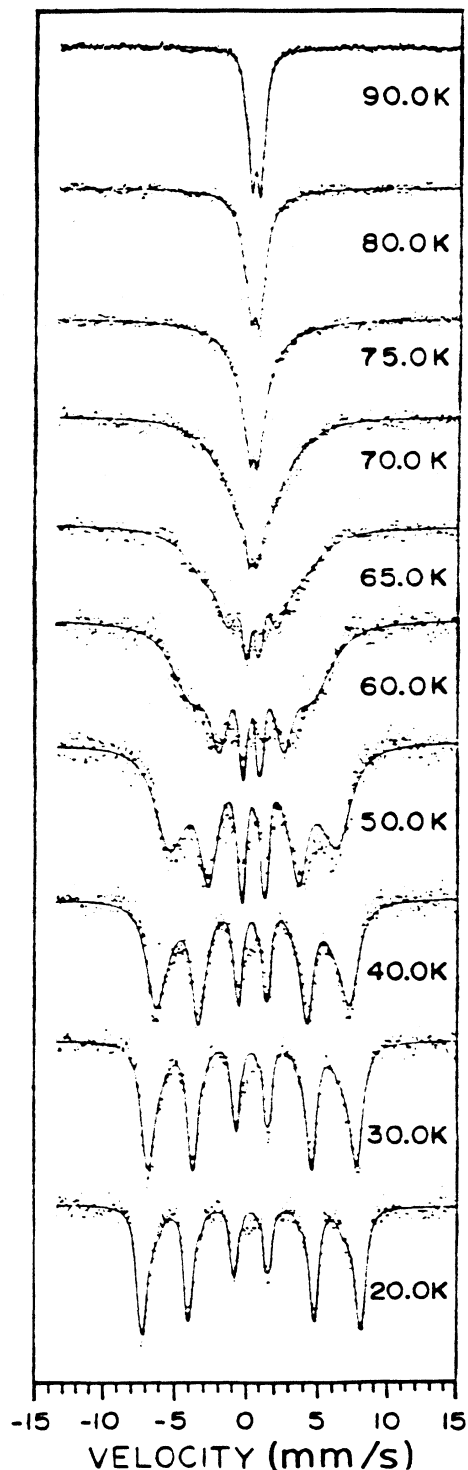

FIG. 5. Mössbauer spectra and least-squares fits for $x = 0.8$.

The samples with $x = 1.2$, 1.6, and 2.0 were remarkable in that a double transition is evident which has apparently not been observed using other methods. Figure 7 shows the spectra and least-squares fits for $x = 1.2$, and Fig. 8 shows the resulting relaxation parameters. Note that the results suggest a double magnetic transition similar to that in the $x = 0.0$ sample. This behavior was found in the $x = 1.6$ and 2.0 samples also, with the transition temperatures decreasing as Sn is added to the system. Note that the $x = 1.2$ sample is adjacent to the $x = 0.8$ sample, which clearly shows a single spin-glass transition. This may be related to the known differences in the crystal structures of $x = 0.0$ and $x = 2.0$ samples, and the results here suggest that perhaps the transition occurs near $x = 1.0$. Clearly more samples in the range $x = 0.8$ and $x = 1.2$ are needed to elucidate the change in properties of this system near $x = 1.0$. The phase diagram for the $BaSn_xTi_{2-x}Fe_4O_{11}$ system based on the Mössbauer results is shown in Fig. 9. The ferrimagnetic phase region is shown in accordance with the magnetic measurements of Iwauchi and Ikeda,[14] and the anomalous phase is indicated with a question mark. This region of the phase diagram had previously been considered paramagnetic,[14] and no discontinuous behavior at $x = 1.0$ was observed in magnetic measurements. It is clear that
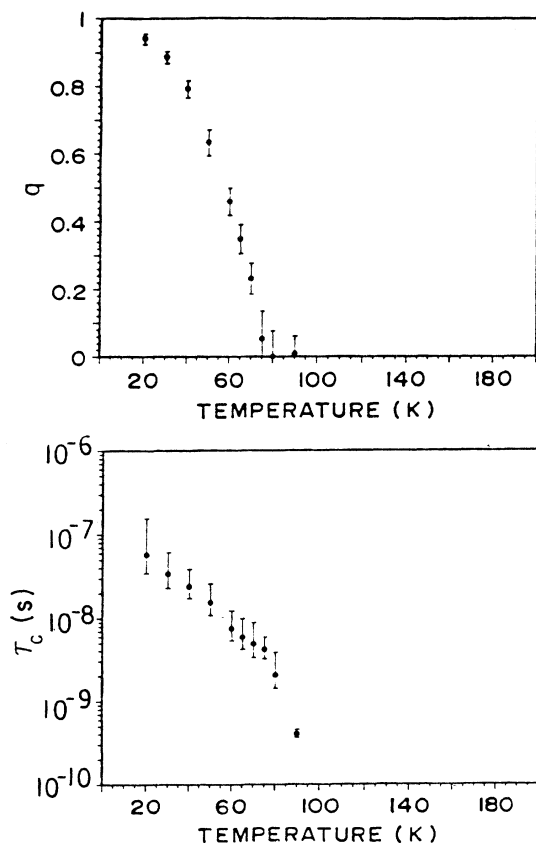

FIG. 6. Order parameter q and spin correlation time τ_c for $x = 0.8$. Note the single spin-glass transition at about 80 K.
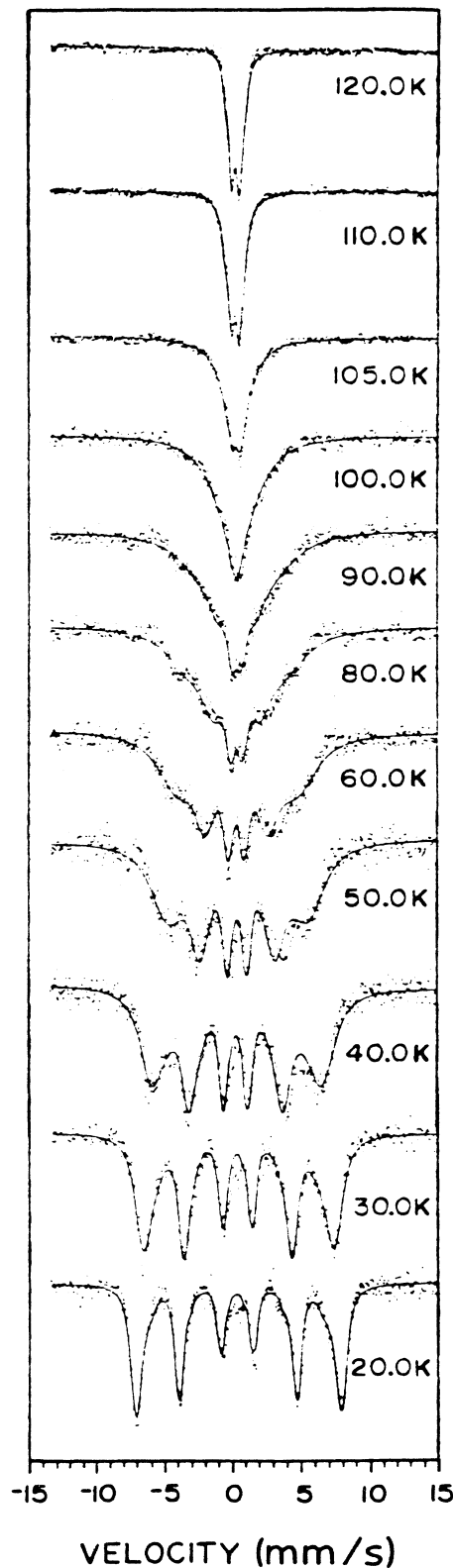

FIG. 7. Mössbauer spectra and least-squares fits for $x = 1.2$. Note that the spectra above 80 K are much broader than for $x = 0.8$.

the upper transitions in the samples with $x > 1.0$ is quite different than that for $x = 0.0$, as a large peak in the susceptibility is not observed for these samples at the upper transition. In any case, it should be noted that the anomalous transition would also be apparent if the spectra were interpreted with hyperfine-field distributions, and the anomaly cannot be considered to be an artifact of the spin-relaxation model.

IV. CONCLUSION

The Mössbauer spectra of samples of $BaSn_xTi_{2-x}Fe_4O_{11}$ with compositions $x = 0.0$, 0.4, 0.8, 1.2, 1.6, and 2.0 were analyzed using a spin-relaxation model to account for the broad line shapes. This analysis is suggested as an alternative to analyses based on distributions of static-hyperfine fields which typically require ten or fifteen free parameters to account for the temperature dependence of the spectra, with little or no physical significance to the fitting parameters. The spin-relaxation analysis suggested here, however, interprets the spectra in terms of key concepts related to the spin-glass transition: spin relaxation and local spin order.

The resulting least-squares fits to the data rival the results obtained on similar systems using distributions of static fields, but require only two free parameters to fit the temperature dependence of the complex spectra, and the parameters have direct physical significance. In addition, the spectra for the samples with $x > 1.0$ indicate the presence of some form of magnetic ordering transition occurring at temperatures above the glass phase which have not been observed with other measurements.

It is worth comparing the calculation of the order parameter q here with methods based on hyperfine-field distributions. Here q is calculated directly from the molecular field parameter. With distributions of static fields, one usually plots the mean or the mode of the distributions, and makes the correspondence with local spin order. Although a large change is sometimes found near the glass temperature, the method is *ad hoc* and does not lend itself well to theoretical interpretation. As far as the spin correlation time τ_c is concerned, the assumption of static fields renders this quantity completely inaccessible in the analysis of the Mössbauer spectra. In contrast, τ_c
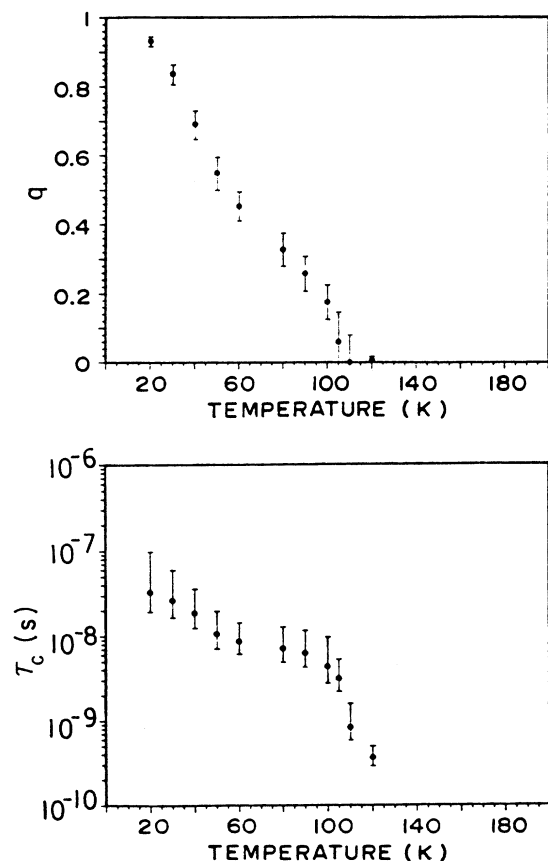

FIG. 8. Order parameter and spin correlation time τ_c for $x = 1.2$. Note the similarity in the temperature dependence of these quantities with the sample with $x = 0.0$ (Fig. 4), which shows a double magnetic transition.
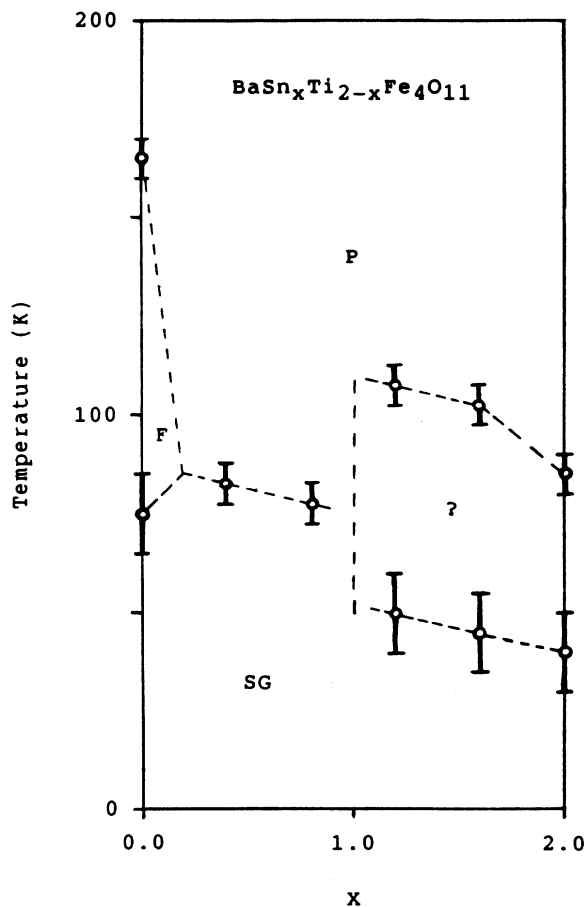

FIG. 9. Magnetic phase diagram for $BaSn_xTi_{2-x}Fe_4O_{11}$ system based on the Mössbauer results. P: paramagnetic, F: ferrimagnetic, SG: spin glass. The anomalous phase is indicated by a question mark. The dashed lines showing the ferrimagnetic region are drawn in accordance with Iwauchi[14] and Ikeda.

is a fundamental quantity in the spin-relaxation viewpoint. We believe this viewpoint is important, as spin glasses are often characterized by their relaxation behavior, in addition to the fact that the μSR results suggest that the assumption of static fields is not warranted in interpreting the complex spectra. Finally, only two free parameters were required to account for the temperature dependence of the complex spectra, as compared with distributions of hyperfine fields which require many free parameters with unknown physical significance in these materials. Unlike many analyses utilizing static-hyperfine-field distributions, the effect of line broadening due to the electric quadrupole interaction and the random spin structure is included to first order.

These results suggest that the large volume of work on spin-glass systems which has utilized static field distributions to interpret the Mössbauer spectra be reconsidered. For example, the broad distributions of static fields extracted from spin-glass spectra have sometimes been used as evidence for the lack of a sharp transition (e.g., second-order phase transition) in these materials, and this point has bred considerable controversy over the years. The present results are consistent with the hypothesis of a sharp transition at the glass temperature, although we are certainly not claiming that this is the case based on this data. Rather, it would appear that the Mössbauer results of spin-glass materials cannot necessarily be used for evidence against the existence of sharp spin-glass transitions. It is likely that other possibly erroneous conclusions have been drawn from the apparently *ad hoc* distributions of static-hyperfine fields, and these analyses should be reconsidered.

The spin-relaxation model proposed here is the simplest applicable to a spin 5/2, and a main goal was to reduce the number of temperature dependent free parameters as much as possible. More complicated models could be devised which include, for example, the effects of crystal fields, or distinctions between the relaxation parameters on the octahedral and fivefold sites. One might also utilize the many-state model of Jones and Srivasta-

va[11] to model the effect of superparamagnetic clusters ("micromagnetism"). It has been suggested,[14] for example, that Ti-rich superparamagnetic clusters (and the effects of Sn to break up these clusters) are important in understanding the magnetic properties of $BaSn_xTi_{2-x}Fe_4O_{11}$. The model used here assumed that the interaction of the atomic spin with its environment was simply due to a spin-freezing molecular field and a perpendicular random field. The results are quite reasonable, however, and it is suggested here that other ferric oxide spin glasses [such as Fe_2TiO_5 (Refs. 1 and 15) and $Mg_{1-t}Ti_tFe_{2-2t}O_4$ (Ref. 3)] can be analyzed the same way. With alterations, models could be devised for other spin-glass systems, such as dilute magnetic alloys (e.g., *Au*Fe alloys), which show similar spectral line shapes. In metallic alloys, the hyperfine-field magnitude is sensitive to the local environment of the Fe atom, unlike ferric oxides, and this would complicate the analysis. One might assume a hyperfine-field distribution to characterize the spectrum far below T_g, and then vary relaxation parameters like h and R to fit the temperature dependence, using (e.g.) a four-state model for spin 3/2. A similar problem may arise with ferrous compounds ($S=2, L=2$), due to orbital contributions to the hyperfine field. This suggests that ferric insulators are the best systems to study using this technique. A similar situation is encountered in Mn^{2+} compounds, which like Fe^{3+} has $S=5/2$ and $L=0$, which makes them especially well understood magnetically.

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