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MÖSSBAUER STUDY IN THIN FILMS OF FeSi₂ AND FeSe SYSTEMS

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MÖSSBAUER STUDY IN THIN FILMS OF FeSi_2 AND FeSe SYSTEMS

INTRODUCTION

The importance of structural studies in thin films using Mössbauer spectroscopy has been discussed in an earlier report [1]. This work is a continuation which includes thin films of FeSi_2 and FeSe . The methods of preparation, characterization, and studying the films as discussed in Reference 1 are used in this study. Thin films of FeSi_2 and FeSe having various thicknesses were deposited and studied to determine the variation of Mössbauer parameters with film thickness. No work on these thin films has been reported thus far.

RESULTS AND DISCUSSION

Thin Films of FeSi_2

In the present work Mössbauer spectra of bulk FeSi_2 and of FeSi_2 thin films having thicknesses 10 Å, 85 Å, 190 Å, 380 Å, and 760 Å deposited on Mylar substrates were taken and a typical spectrum is presented in Figure 1. Only two lines could be fit to the spectrum in all cases. As discussed in the case of FeTe films [1], it is improbable that a material which shows one non-cubic site in bulk [2] would show two nonequivalent cubic iron sites in thin films deposited on a substrate which is amorphous and therefore does not influence the film structure. Since, in case of bulk FeSi_2 a quadrupole split spectrum was observed, the two lines observed in thin films are attributed to quadrupole doublets. The parameters of the doublets are given in Table 1.

Table 1 indicates that the isomer shift (IS) values of these doublets show a decrease with increasing thickness and are constant beyond 190 Å. The initial decrease in the IS value is indicative of an increase in the s-electron density at the iron site with increasing film thickness. The 4s electron contribution to iron coming from silicon ions increases when the number of Si near neighbors increases, or when the Fe-Si distance decreases [3]. At low thicknesses the dangling bond density is high. This leads to a lowering of the number

of Si near neighbors for some iron sites. As a result, a lowering of the s-electron density at these iron sites could be possible. The other possible reason for the observed behavior of IS values could be that the Fe-Si distances for low thickness films are greater than those for films of higher thicknesses. On the basis of IS variation alone, it is difficult to say which phenomenon is playing the dominant role. However, quadrupole splitting (QS) data, as indicated below, favor greater Fe-Si distances at lower thicknesses.

It is observed that the QS values show a gradual increase with increasing film thickness (Table 1) to 380 Å thickness. Variation in QS values could be due to either of the two causes previously discussed. Presence of dangling bonds would, however, mean more distorted silicon polyhedra and hence a larger QS value at lower thicknesses [3]. However, an increase of Fe-Si distance would mean a reduction in the quadrupole interactions between the iron ion and the silicon polyhedra. It is possible that both these effects are present; however, since the net observed effect in low thickness range is a decrease in the QS value with decreasing thickness, it is concluded that changes in Fe-Si distances play the dominant role at lower thicknesses. Such changes in lattice constants at very low thicknesses have been reported by other workers [4]. The decrease of QS values at 760 Å is indicative of disappearance of dangling bonds. This is supported by the fact that QS values for the 760 Å film and the bulk FeSi₂ are equal. The asymmetries of line widths and areas corresponding to the two lines of the doublets do not show any consistent variation with thickness, perhaps because these asymmetries originate from multivarious causes previously discussed. No definite conclusion in this regard can be drawn without further investigations involving study at different temperatures.

The Mössbauer spectrum of 100 Å FeSi₂ film deposited on aluminum did not show any quadrupole splitting; a single line corresponding to an IS value of 0.0051 ± 0.0142 mm/s was observed. It may be pointed out that the FeTe films deposited on aluminum substrate had also exhibited a single line [1] with an IS value close to the one observed in the present case. It is therefore concluded that even if the structure and bond nature in the respective bulks are different, their thin films deposited on aluminum substrates show a lot of structural similarity. This observation reflects on the influence of substrate on film structure.

Thin Films of FeSe

Bulk and thin films of FeSe having thicknesses of 500 Å, 1000 Å, and 2000 Å deposited on aluminum substrate were studied. The computer fits of one of the spectra is shown in Figure 2. The observed Mössbauer parameters are given in Table 2. The lines, though broadened, could not be split.

The large line width in the present case can be due to (1) the presence of small internal field [2] and (2) the disorder due to dangling bonds [1]. Any variation in line width reflects on the variation of the two factors. From earlier studies, it is well-known that the relaxation effects appear in low-thickness films and that below a few-angstrom thickness the hyperfine field completely disappears. The present study was confined to a higher range of thickness where such relaxation effects would be absent. The presence of any magnetic field in such samples may result in line broadening, but the variation in the width of Mössbauer lines with film thickness cannot be due to any change in the magnitude of the field.

The other factor that can cause line broadening is the dangling bond disorder. As explained in the case of thin films of FeTe [1], the disorder due to dangling bonds becomes less as the film becomes thicker. The observed decrease in the line width suggests the lowering of disorder due to dangling bonds. The observation that at 2000 Å the line width is close to that of the bulk shows that the dangling bond disorder disappears at this thickness. At 2000 Å and above, the broadening W_M being due to hyperfine interactions only [2], an estimate of the broadening due to disorder at lower thicknesses can be made. The observed line width W_a can be written as

$$W_a = W_N + W_M + W_D + W_T \quad ,$$

where W_N is the natural line width from life time considerations, W_M is the broadening due to hyperfine field, W_T is the broadening due to absorber thickness, and W_D is the broadening due to disorder. Taking the values of $W_N + W_M + W_T$ as 0.70 mm/s (line width of 2000 Å thickness), W_D was calculated for 500 Å and 1000 Å thick films (Table 2). It is possible to correlate the width of Mössbauer line with the dangling bond configuration.

The IS values are almost constant for all film thicknesses (Table 2). This is due to the fact that the present study was confined to films of high thickness only (≥ 500 Å). It was observed from our studies on FeTe [1] and FeSi₂ systems that beyond a certain thickness [2], the IS values do not change appreciably. This is because in films of higher thickness the dangling bond density is low and it does not vary much with film thickness. A small number of dangling bonds present at these thicknesses will change the local order at

some of the iron sites and hence would cause broadening in the line. However, their number is not large enough for them to be present at all the iron sites so as to cause an overall change in the IS value. Moreover, in the present case the films were deposited on aluminum substrate. The crystalline aluminum substrate plays a dominant role in the formation of bonds in the films; the crystalline structure guides the initial bonds in the film, and this bond configuration is maintained even for higher film thicknesses. This again explains why the IS value does not change with thickness. Since the influence of the substrate is absent in bulk, the observed IS values in films differ appreciably from that of the bulk [2].

The IS values observed in case of FeSe films are very close to the values observed for FeTe and FeSi₂ (Table 2) deposited on the same substrate (aluminum). It is interesting to note that the nature of the spectra in all these cases is almost identical. They all show a single line with no indication of any quadrupole interaction. The cubic structure of the aluminum substrate is maintained in the films even for thickness as high as 1000 Å (in case of FeTe) [1].

CONCLUSION

In conclusion, on the basis of the present study it is felt that Mössbauer spectroscopy throws light on certain aspects of thin film structure which never before had been emphasized by the traditional methods of study. This kind of structural study gives a clearer picture of dangling bond configuration and nature of bonds in films.

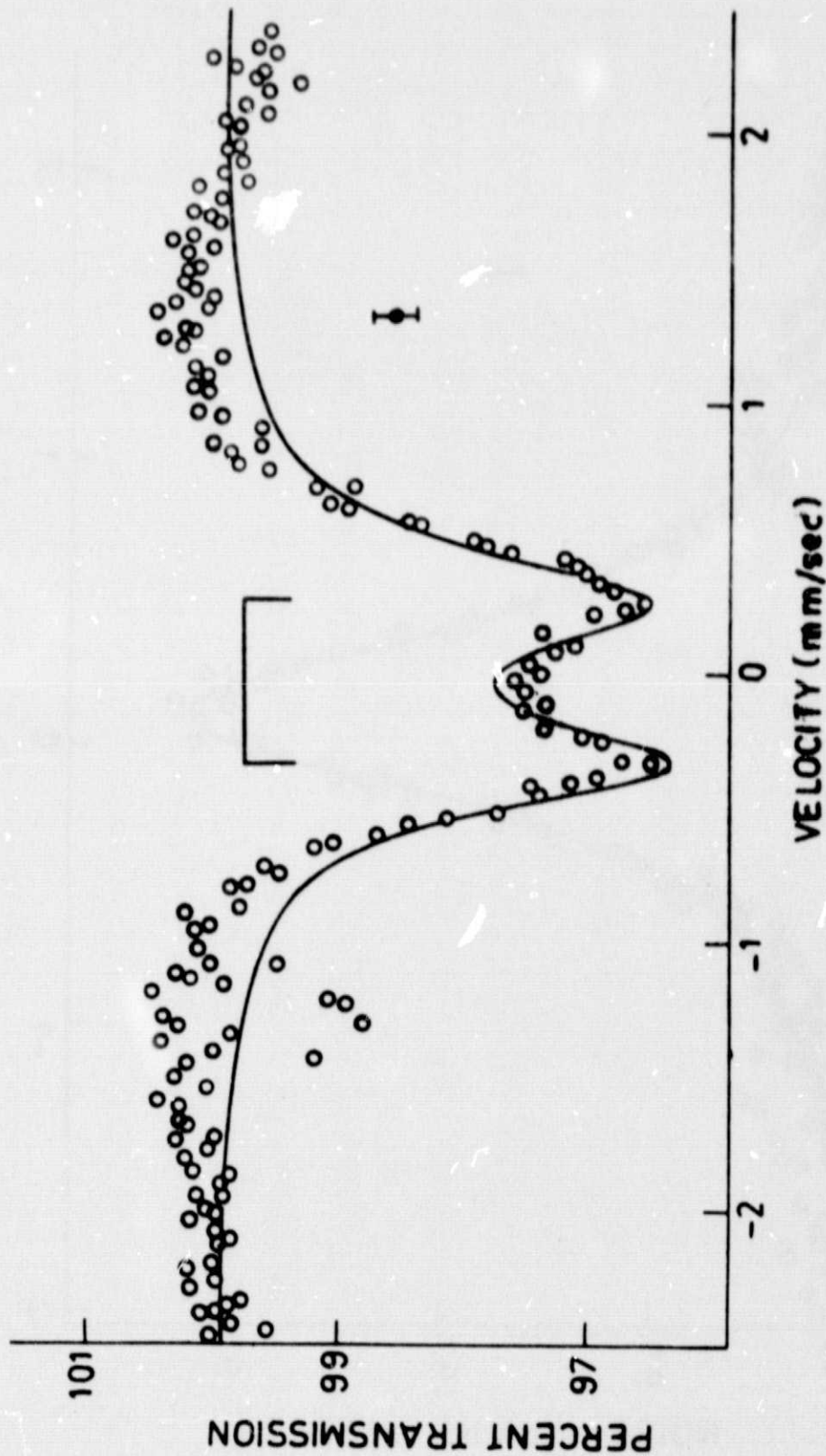


Figure 1. Mössbauer spectrum of FeSi_2 film (85 Å).

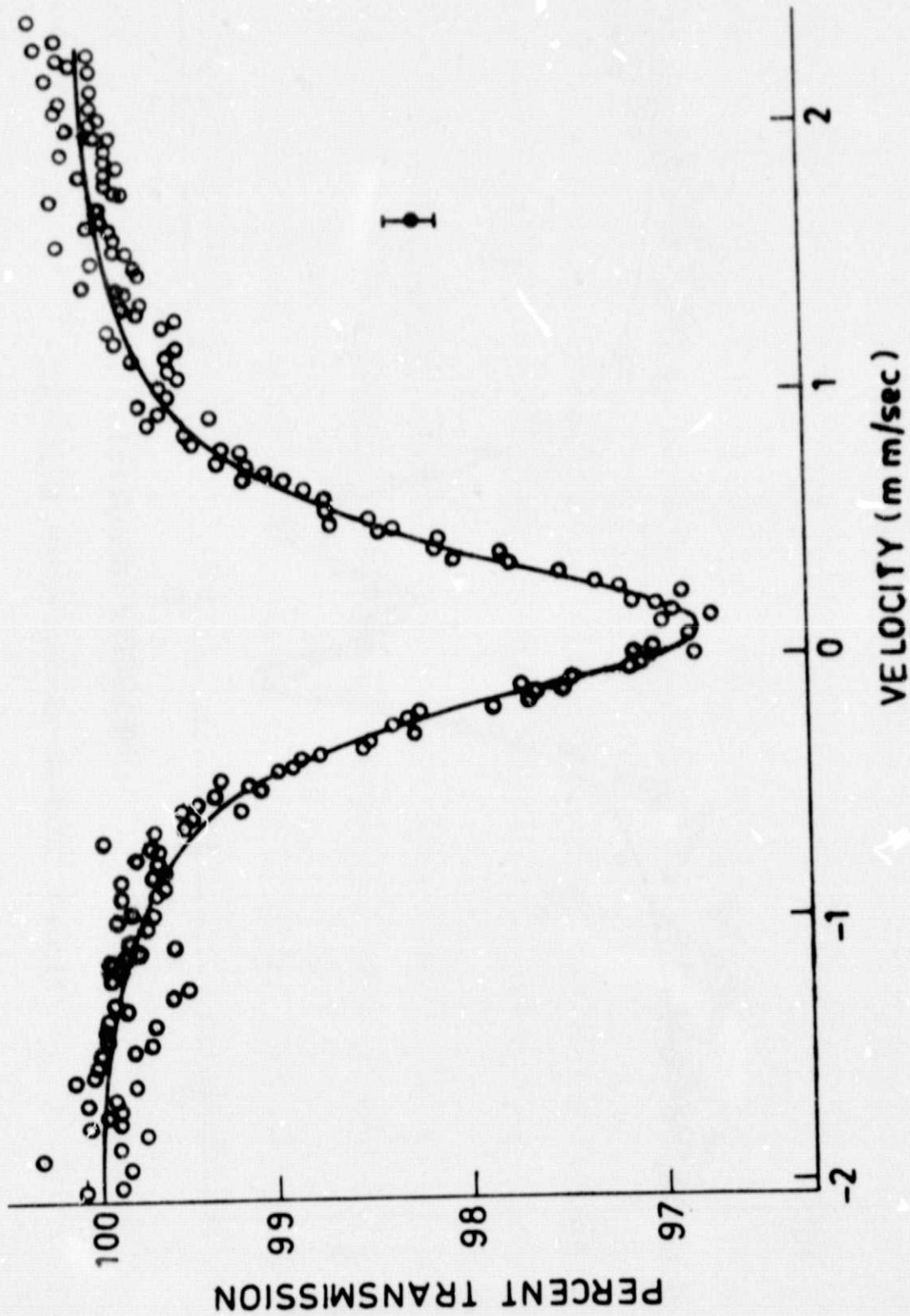


Figure 2. Mössbauer spectrum of FeSe film (2000 Å on aluminum substrate).

TABLE 1. MÖSSBAUER PARAMETERS IN FeSi₂ SYSTEM
(FILMS ON AMORPHOUS SUBSTRATE)

Thickness (Å)	\bar{E} (mm/s)	QS (mm/s)
10	0.152 ± 0.038	0.584 ± 0.042
85	-0.036 ± 0.042	0.604 ± 0.047
190	-0.017 ± 0.050	0.665 ± 0.05
380	0.010 ± 0.028	0.745 ± 0.032
760	-0.004 ± 0.021	0.655 ± 0.026
Bulk	-0.022 ± 0.019	0.606 ± 0.023

TABLE 2. MÖSSBAUER PARAMETERS OF FeSe SYSTEM
(FILMS ON ALUMINUM SUBSTRATE)

Film Thickness (Å)	IS (mm/s)	W _a (mm/s)	W _D (mm/s)
500	0.074 ± 0.020	0.971 ± 0.042	0.208
1000	0.126 ± 0.033	0.909 ± 0.046	0.146
2000	0.113 ± 0.012	0.763 ± 0.012	
Bulk	0.204 ± 0.011	0.706 ± 0.013	