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The effect of the methods of preparation on the Mössbauer spectrum of an Fe–Ge intermetallic compound

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A comparative study was carried out on the effect of the methods of preparation on the Mössbauer spectrum of the β-Fe_5Ge_3 phase. The disagreements between the various reported spectra for the β-phase can be attributed to variations in the stochiometry of the final product. Sintering seems to be the best way to prepare the β-phase, while melting of the iron–germanium powders resulted in evaporation and considerable loss of germanium. The various methods of preparation were subjected to chemical analysis and X-ray diffraction.

1. Introduction

The iron–germanium alloy system is an interesting one for the study of electronic and magnetic properties of intermetallic compounds. This system contains several phases having different magnetic properties [1–3]. The β-Fe_5Ge_3 phase is ferromagnetically ordered below 500 K [3] and its easy direction of magnetization is the crystallographic *a*-axis [4]. The physical properties of the β-Fe_5Ge_3 phase has been the subject of many investigations and controversies [2–20]. The β-Fe_5Ge_3 phase has a structure of the $B8_2(Ni_2In)$ type and there are two kinds of iron sites: the $2a(0,0,0,;0,0,\frac{1}{2})$ and the $2(d)$ $(\frac{1}{3},\frac{2}{3},\frac{3}{4};\ \frac{2}{3},\frac{1}{3},\frac{1}{4})$ sites which are occupied by 2 and 1.33 iron atoms, respectively [5]. The magnetic properties of this phase were studied by Mössbauer spectrum analysis as well as by other research methods. There are disagreements between the reported spectra for the β-Fe_5Ge_3 phase. It seems that the Mössbauer spectrum observed depends very much on the methods used by various investigators to prepare this compound. The purpose of this investigation was to study the effect of the method of preparing the β-Fe_5Ge_3 intermetallic phase on the resultant Mössbauer spectra, while the exact composition of the alloy was verified by chemical and X-ray analysis.

2. Experimental procedure

Sintered and vacuum-cast specimens were prepared from powdered electrolytic iron (99.999%) and germanium (99.99%) in the ratio which corresponds to the β-Fe_5Ge_3 phase [1]. After sizing, mixing and compacting the powders at 598 MPa, the mixtures were placed in evacuated quartz capsules and sintered isothermally under vacuum for different lengths of time at 600 and 800° C. The preparation methods as reported by other authors were also used and the resultant spectra compared. Following Bhide and Date [9], specimens were prepared by: "melting the required proportions of spectrographically pure iron and germanium in an alumina crucible in the induction furnace." Utilizing the Yamamoto method of preparation [8]: "Iron and germanium powders were mixed in the desired proportions and were sealed in evacuated silica tubes. The alloy was sintered at 1000° C for 2 days and then quenched in water. The alloys thus obtained were crushed into powder and sintered again in evacuated silica tubes for 2 days. The β-Fe_5Ge_3 phase was obtained by annealing the sintered alloy at 800° C for 20 h and then quenched in water." Repeating the method of Germagnoli *et al.* [15]: "Specimens were sintered at 800° C and then the mixture was melted in an induction furnace in vacuum."

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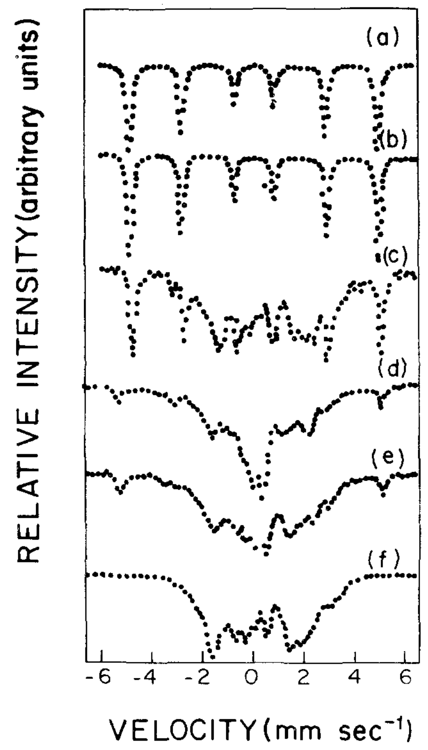

Figure 1 Fe^{57} Mössbauer spectra at room temperature of specimens sintered at 600° C over different periods of time, (a) before sintering, (b) 10 min (only α-Fe), (c) 20 min, (d) 35 min, (e) 50 min and (f) 120 min.

All samples obtained by the various methods of preparation were subjected to chemical analysis and X-ray diffraction by the Debye–Scherrer method, using a CoKα radiation source. The same powder was used for Mössbauer spectroscopy, using an Elscint type 30 computerized spectrometer with a 25 mci source of Co^{57} in a Pd matrix for the 14.4 keV γ-line of the Fe^{57} nuclei. In these experiments, the breadth of the inner resonance line of α-iron was found to be 0.25 mm sec^{-1}.

3. Results and discussion

Fig. 1 shows a series of room-temperature Mössbauer spectra of mixtures with the composition of the β-Fe_5Ge_3 phase, for different sintering times up to the completion of the reaction. In the sintering process at 600° C, the following phases were identified by X-ray diffraction and Mössbauer spectroscopy: α-FeGe, ϵ-Fe_3Ge, β-Fe_5Ge_3, η-Fe_xGe, with the β-Fe_5Ge_3 phase being the final and only product present at the end of 120 min of sintering time. After 120 min Fe_5Ge_3 was present in the pure form and further sintering, up to 50 days, (see Fig. 2), did not affect the spectrum. The small fluctuations that were observed in the spectra were attributed to the nonstoichiometric character of the β-phase. It should be noted that the various phases were identified at an earlier stage, and with better clarity, by Mössbauer spectroscopy. The kinetics of formation of the β-Fe_5Ge_3 phase during isothermal sintering is discussed elsewhere [21]. Sintering the pure iron and germanium powders to the final β-Fe_5Ge_3 phase was very fast at 800° C and it required only 10 min to complete the reaction. Further sintering at 800° C did not affect the spectrum as shown in Fig. 2 (as is the case of sintering for longer periods of time at 600° C).

When the preparation methods reported in the literature by other investigators [8, 9, 15] were followed, spectra very similar to those reported by others were observed. The observed spectra were different from the spectrum obtained in this study for the sintered β-Fe_5Ge_3 phase.

The room-temperature Mössbauer spectrum of this study, depicted in Fig. 3 and summarized in Table I, revealed that the Fe_I component on the 2(*a*) lattice site has hyperfine splitting of 123 kOe and that the Fe_{II} component on the 2(*d*) lattice sites has two hyperfine splittings of 188 kOe and 224 kOe. The room-temperature isomer shift was 0.30 ± 0.04 mm sec^{-1} for both the 2(*a*) and 2(*d*) sites. Bhide and Date [9], who prepared the β-Fe_5Ge_3 phase by melting, reported a completely different room-temperature Mössbauer spectrum from the one observed by us. They observed that the hyperfine magnetic fields at the 2(*a*) and 2(*d*) sites are 315 ± 10 kOe and 185 ± 10 kOe, respectively. Germagnoli *et al.* [15], who prepared their compound by sintering at 800° C and subsequent melting, reported that the hyperfine magnetic fields at the 2(*a*) and 2(*d*) sites were 257 ± 15 kOe and 207 ± 10 kOe, respectively. The isomeric shifts are 0.10 mm sec^{-1} for the 2(*a*) site and 0.15 mm sec^{-1} for the 2(*d*) site. Table I summarizes the results of this study for the sintered β-Fe_5Ge_3 phase and compares them to those obtained by other investigators [8, 9, 15], who used similar and different methods of preparation. Fig. 4 shows the liquid nitrogen temperature Mössbauer spectrum for the β-Fe_5Ge_3 phase. The spectrum was identical for the various samples of the β-phase which were prepared at the different sintering temperatures as described previously. The spectrum shows superposition of different

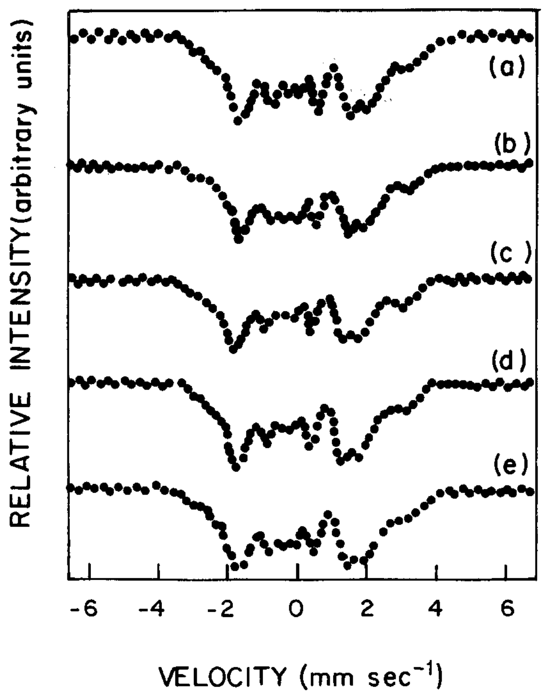

Figure 2 Fe^{57} Mössbauer spectra at room temperature for specimens sintered at 600° C over different periods of time, (a) 120 min, (b) 24 h, (c) 48 h, (d) 120 h and (e) 50 days.

hyperfine splitted magnetic components due to the two non-equivalent sites for the Fe^{57} nucleid. The Fe_I component on the 2(*a*) lattice sites has an hyperfine magnetic field of 137 kOe and the isomer shift is 0.32 mm sec^{-1}. The Fe_{II} component on the 2(*d*) lattice sites results from two hyperfine magnetic fields; one of 213 kOe and the other of 264 kOe. The isomer shifts are 0.27 mm sec^{-1} and 0.2 mm sec^{-1}, respectively. The results of this investigation are in very good agreement with those of Yamamoto [8], who also prepared the β-Fe_5Ge_3 phase by sintering. Our attempt to prepare the β-Fe_5Ge_3 phase by casting or by sintering and casting showed a persistent loss of germanium. When the method of casting used by Bhide and Date [9] was followed a considerable loss of germanium was noticed. Whilst preparing the specimens by sintering (as previously described), no germanium loss was observed. Other investigators [2, 22, 23], prepared the β-Fe_5Ge_3 phase as part of an effort to construct the Fe–Ge phase diagram. A loss of germanium due to its evaporation was observed when the β-phase was prepared by melting in an arc furnace under 1 atm of argon. Jolly and Latimer [24] also indicated that iron and germanium powders can contain as much as 5 wt% oxygen unless these powders are especially prepared. The presence of oxygen during the preparation of any Fe–Ge compound may lead to the formation of the $GeFe_2O_4$ compound which, in itself, will affect the Mössbauer spectrum. No significant loss of germanium was found when fusion was carried out in evacuated and sealed quartz tubes but losses of germanium were observed when fusion was carried out under dynamic vacuum [2, 22]. The very good agreement between the Mössbauer spectra observed

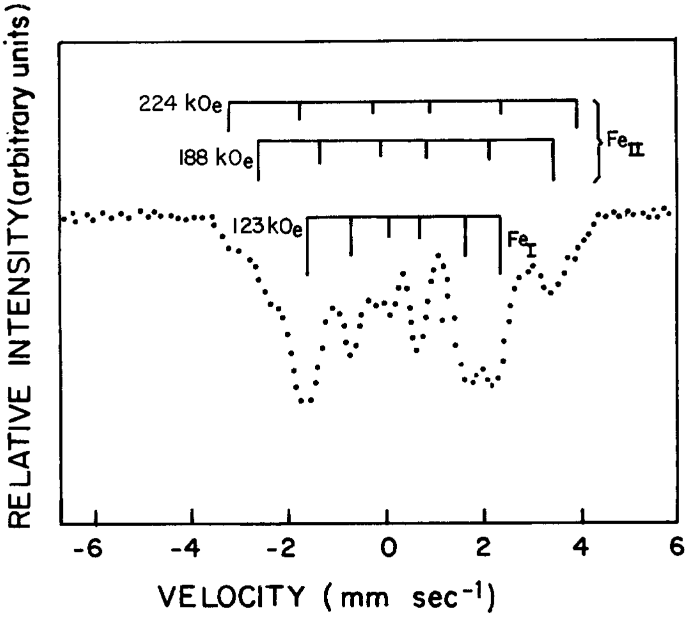

Figure 3 Fe^{57} Mössbauer spectrum for the β-Fe_5Ge_3 phase at room temperature.

TABLE I Mössbauer parameters of the β-Fe_5Ge_3 phase as reported by others and observed by us

Investigator	Method of preparation	Testing temperature (K)	Hyperfine magnetic field (kOe)	Isomer shift (mm sec^{-1})	Quadrupolar splitting (mm sec^{-1})
H. Yamamoto [8]	Sintering	80	Fe_I 136 Fe_{II} 214 256	–	–
Bhide and Date [9]	Casting	300	Fe_I 315 ± 10 Fe_{II} 185 ± 15	–	–
Germagnoli *et al.* [15]	Sintering and casting	300	Fe_I 257 ± 15 Fe_{II} 207 ± 10	0.10 0.55	
This work	Sintering	300	Fe_I 123 Fe_{II} 188 224	0.30 0.30 0.30	0.8
		80	Fe_I 137 Fe_{II} 213 264	0.32 0.27 0.20	0.10

by us and Yamamoto [8], and the disagreement with the Mössbauer spectra observed by others [9, 15], can be attributed to the methods of preparation of the material examined. When it was attempted to prepare the alloy by melting a loss of up to 25 wt% germanium was noticed. This was due to the high vapour pressure of molten germanium. It seems that when the specimens were prepared by melting the result was an alloy which did not have the composition of the β-Fe_5Ge_3 phase and this was probably the reason for the disagreement between the spectra of the sintered compound and the spectra of whatever composition was present after melting the germanium. The results obtained in this work indicate that the different production methods of the β-phase are significant in view of the fact that they result in different Mössbauer spectra for the same phase. The method of preparation greatly affects the final composition of the compound and starting with stochiometrically mixed components does not guarantee the desired final compound. Many of the discrepancies about the β-Fe_5Ge_3 phase found in the literature can be explained by the different production methods.

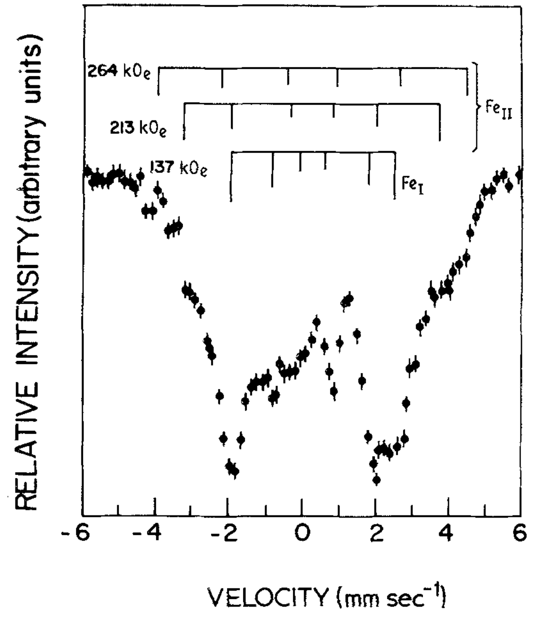

Figure 4 Fe^{57} Mössbauer spectrum for the β-Fe_5Ge_3 phase at liquid nitrogen temperature.

4. Conclusions

The different production methods of the β-phase results in different Mössbauer spectra for the same phase. Sintering of iron–germanium powders seems to be the best way to prepare the β-Fe_5Ge_3 phase. Melting of the powders causes considerable evaporation of germanium thus resulting in deviation from the desired composition of the prepared product. The results of this investigation re-emphasize the fact that careful preparation and examination of the composition of the final product is necessary before any further studies are undertaken.

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