

THE UNIVERSITY OF MANITOBA

THE MAGNETIC PROPERTIES OF
 β -PHASE IRON-GERMANIUM

by

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the University of Manitoba in partial fulfillment of the requirements
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ABSTRACT

A study of the magnetic properties of the hexagonal β -phase or iron germanium was carried out in an attempt to resolve some of the conflicts which existed in the literature.

Three polycrystalline samples were prepared containing enriched iron and Mössbauer measurements were carried out from 4.2 K to above the Curie temperature. The results obtained consisted of several broadened overlapping spectra and it was felt that more information was required to obtain a unique interpretation.

A single crystal was then grown with composition $\text{Fe}_{1.67}\text{Ge}$. It was found to have an easy magnetization plane in the basal plane and a hard direction along the c-axis. Aligned Mössbauer absorbers were made with the c-axis in the absorber plane and with the c-axis perpendicular to the absorber plane. Measurements in applied fields of up to 50 kOe gave spectra with considerably improved resolution.

The spectra were fitted initially assuming three component six-line spectra and the hyperfine field was found to be anisotropic. Values of electric field gradient and isomer shift were determined for the three component spectra.

Magnetization and x-ray measurements were also carried out and gave results in agreement with those obtained for polycrystalline samples.

Previous results for the β -phase had been interpreted on the basis of two different models for the distribution of atoms. The Mössbauer spectra and x-ray diffraction patterns were found to favour the model in which iron atoms were on two sites only. Proposals by previous authors that the atomic spins were canted were rejected on the basis of the measurements in applied fields.

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TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	1
ACKNOWLEDGEMENTS	2
1. INTRODUCTION	
1.1 General	7
1.2 Phase diagram	7
1.3 Crystal structure	9
1.4 Magnetic moments	10
1.5 Mössbauer spectra	11
1.6 Anisotropy measurements	14
1.7 Preliminary conclusions	14
2. SAMPLE PREPARATION	
2.1 Method of preparation	15
2.2 Heat treatment	15
2.3 Sample purity	18
2.4 The effect of cooling rate on $\text{Fe}_{1.95}\text{Ge}$	20
2.5 ϵ -phase	24
2.6 Single crystal	24
3. MAGNETIZATION MEASUREMENTS	
3.1 Magnetization equipment	26
3.2 Measurements	26
3.3 Results	28
3.4 Conclusions	32
4. MÖSSBAUER MEASUREMENTS	
4.1 Mössbauer equipment	34
4.2 Mössbauer absorbers	37

TABLE OF CONTENTS (cont'd)

	<u>Page No.</u>
4. MÖSSBAUER MEASUREMENTS (cont'd)	
4.3 Fitting program	37
4.4 Measurements as a function of temperature	39
4.5 Aligned absorbers	44
4.6 Spectra above the Curie temperature	49
4.7 Spectra below the Curie temperature	51
4.8 Spectra in an applied magnetic field	53
5. DISCUSSION	
5.1 Mössbauer effect	56
5.2 Component spectra	60
5.3 Directions of the atomic magnetic moments	61
5.4 Electric field gradient	63
5.5 Isomer shift	65
5.6 Hyperfine field	66
5.7 Distribution of atoms	67
6. CONCLUSIONS	77
REFERENCES	79

LIST OF FIGURES

Page No.

1.1	Phase diagram of the iron germanium system	8
2.1	Lattice parameters for the β -phase as a function of composition	19
2.2	The diffraction pattern of $\text{Fe}_{1.95}\text{Ge}$ for various quench rates	22
2.3	The Mössbauer spectra of $\text{Fe}_{1.95}\text{Ge}$ for various quench rates	23
3.1	Magnetization measurements on $\text{Fe}_{1.67}\text{Ge}$	27
4.1	Block diagram of Mössbauer spectrometer	35
4.2	Mössbauer spectrum for iron foil calibration sample.	38
4.3	Mössbauer spectra of $\text{Fe}_{1.55}\text{Ge}$ as a function of temperature	40
4.4	Mössbauer spectra of $\text{Fe}_{1.7}\text{Ge}$ as a function of temperature	41
4.5	Mössbauer spectra of $\text{Fe}_{1.95}\text{Ge}$ as a function of temperature	42
4.6	Computer fit to $\text{Fe}_{1.95}\text{Ge}$ at room temperature	43
4.7	Curie temperature measurement	44
4.8	Measured values of Curie temperature	44
4.9	Mössbauer spectra of aligned absorbers of $\text{Fe}_{1.67}\text{Ge}$	54
5.1	Computer fit to $\text{Fe}_{1.67}\text{Ge}$ at room temperature with an applied field of 50 kOe along the c-axis.	76

LIST OF TABLES

		<u>Page No.</u>
1.1	Magnetic moments in μ_B attributed to the 2(a) and 2(d) sites	12
3.1	Saturated magnetization values	29
4.1	Parameters obtained from two-line computer fits to Mössbauer spectra above the Curie temperature	50
4.2	Range of parameters consistent with spectrum of $Fe_{1.67}Ge$ above the Curie temperature	52
4.3	Parameters obtained from computer fits to Mössbauer spectra of aligned absorbers, assuming three component spectra.	55
5.1	Electric field gradient and isomer shift for the three component spectra	64
5.2	Hyperfine field of the three component spectra for different orientations reduced to zero applied field. Calculated dipolar fields and measured anisotropy fields.	68
5.3	A comparison of calculated x-ray line intensities with published experimental values	70
5.4	The neighbours of each site	72
5.5	Probabilities of different distributions of nearest neighbours for Daniels' hypothesis for $Fe_{1.68}Ge$.	74

CHAPTER 1

INTRODUCTION

1.1 General

The β -phase of iron germanium has been the subject of investigation and controversy during the last twenty years especially with regard to its magnetic properties. There is a large number of conflicting experimental results and in turn interpretations differ widely. It was hoped that by carrying out magnetization and Mossbauer measurements backed up by x-ray analysis over a wide range of temperatures and making use of an applied magnetic field a consistent interpretation of the experimental results might be obtained. The following chapters report on this study. A review of the results obtained by other investigators is given in this chapter, several of them will be considered again later in comparison with the results obtained in this study.

1.2 Phase diagram

The existence of the β -region in the phase diagram of the iron-germanium system was first reported by Hansen (1) in 1958 on the basis of work done by Ruttewit and Masing (2). The crystal structure was determined to be $B8_2(Ni_2In)$ (33) by Laves and Wallbaum (3) also by Castelliz (4). The first magnetic investigation was reported by Yasukochi Kanematsu and Ohoyama (5) who carried out magnetization measurements as a function of temperature and found the β -phase to be ferromagnetic.

Since that time papers have appeared reporting further phase diagram refinements based on magnetization and x-ray measurements. The phase diagram now generally accepted as far as the β -phase is concerned was

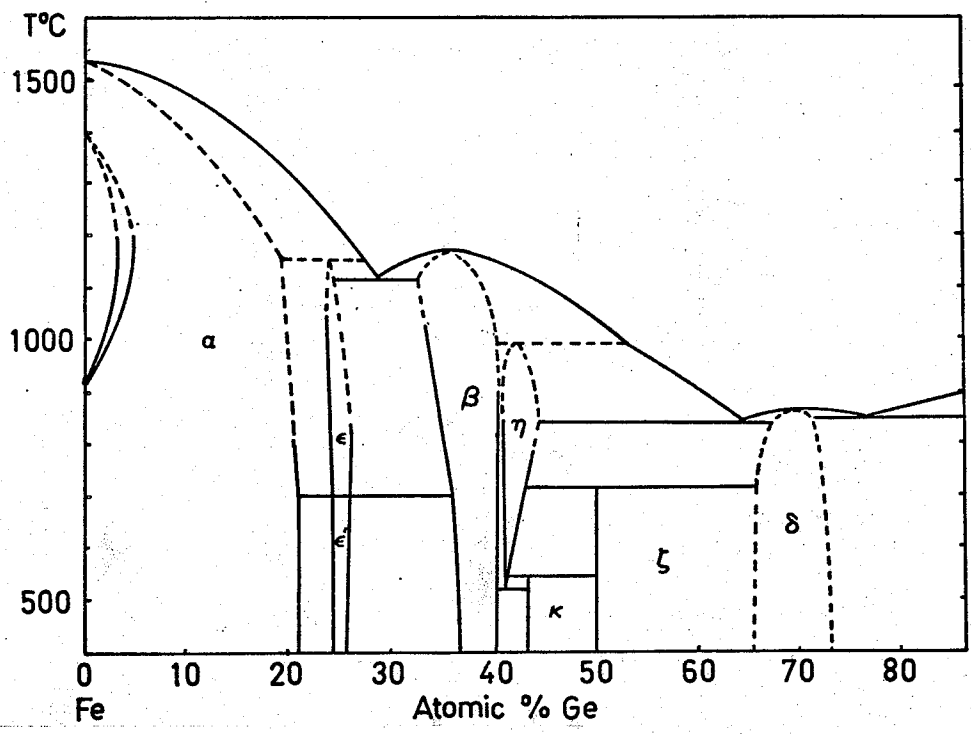


Fig. 1.1 Phase diagram of the iron germanium system

reported by Kanematsu and Ohoyama (6) and it is reproduced in figure 1.1. It can be seen that extreme members of the phase lie at atomic compositions corresponding to Fe_2Ge and $\text{Fe}_{1.5}\text{Ge}$ while at a composition corresponding to Fe_5Ge_3 the phase extends to temperatures up to the melting point of $\approx 1200^\circ\text{C}$. It can also be seen that the neighbouring phase at higher iron concentration is a mixture of β - and hexagonal ϵ -phase Fe_3Ge . The other neighbour is a narrow mixed phase of β - and η -phase which is a modification of β .

1.3 Crystal Structure

X-ray diffraction lines from β -phase samples may be indexed assuming a hexagonal B8_2 structure (33). Pycnometric density measurements indicate approximately 2 formula units per unit cell for Fe_xGe (7). There are three different sites, the unit cell containing two of each. The positions are 2(a) at 0,0,0 and 0,0,1/2, 2(d) at 1/3, 2/3, 3/4 and 2/3, 1/3, 1/4, and 2(c) at 1/3, 2/3, 1/4 and 2/3, 1/3, 3/4. The lattice parameters obtained vary over the composition range as follows: $a = 3.99 \text{ \AA}$ to 4.04 \AA and $c = 4.99 \text{ \AA}$ to 5.02 \AA giving an axial ratio of 1.25.

In order to determine the distribution of atoms over the available sites, Kanematsu assumed a model as follows. The germanium atoms go onto the 2(c) sites. Then the iron atoms fill first the 2(a) sites and then the 2(d) sites. Thus if there are two formula units per unit cell, both the 2(c) and the 2(a) sites will be fully occupied with germanium and iron atoms respectively, whereas the 2(d) sites will contain iron atoms and vacancies. Where density measurements indicated deviations from exactly 2 formula units per unit cell any 2(c) sites remaining unfilled

with germanium atoms would be filled with iron atoms. Alternatively any remaining germanium after the 2(c) sites were filled would go onto the 2(a) sites. Kanematsu's x-ray intensities calculated on the basis of this model are in good agreement with the observed intensities as are those of Adelson and Austin (8) for the same model. They were also able to reject several alternative postulates for atomic distribution. The above distribution of atoms is now generally accepted but has recently been called into doubt by Daniels et al (9) who, unable to fit their Mössbauer spectra on the basis of two iron positions, propose that the 2(a) sites are filled with iron and the remaining iron and germanium atoms are distributed on both the 2(d) and 2(c) sites leaving vacancies on both. Unfortunately they do not calculate diffracted x-ray intensities predicted by their model.

Laue photographs of single crystals have been made by several authors (9-11) and there appears to be some evidence for small distortion.

1.4 Magnetic Moments

There is wide disparity among assignments of magnetic moments to the iron atoms within the unit cell by different authors.

Kanematsu (12) deduced magnetic moments from magnetization data. He measured magnetization as a function of temperature for samples over a range of compositions and deduced the saturated ferromagnetic moment extrapolated to 0°K. From the slope of the inverse susceptibility above the Curie temperature he obtained the paramagnetic moment. The results he obtained are average values for the two sites but from the way in which these moments change with increasing occupancy of the 2(d) sites, values of magnetic moment can be assigned to the atoms on the two different

sites. His results are shown in table 1.1. (In the case of paramagnetic moments, values of gS are given instead of $g\sqrt{S(S+1)}$ for ease of comparison with the ferromagnetic moments). The difference between the ferromagnetic and paramagnetic moments on the 2(a) sites caused Kanematsu to propose a model in which the 2(a) sites had half the spins in one direction and the other half almost in the opposite direction while the 2(d) site spins were almost parallel. The experimental values contradicted an earlier prediction by Kanematsu (13) the results of which are also shown. Atomic spins were deduced by considering co-valent bonds formed by hybridized orbitals in an application of the ideas of Goodenough (14).

Neutron diffraction experiments have also been carried out in an attempt to deduce the atomic spins. The room temperature values are also shown in table 1.1. Katsuraki (10) and Forsythe and Brown (11) carried out measurements on single crystals using the polarized neutron technique. The neutron diffraction experiments of Adelson and Austin (8) were carried out on both single crystals and powdered polycrystalline samples.

From table 1.1 it can be seen that there is little agreement among magnetization and neutron diffraction data even as to which site has the greater magnetic moment. For this reason a number of investigators carried out Mössbauer measurements.

1.5 Mössbauer Effect Measurements

The first Mössbauer spectrum was reported by Yamamoto (15) in 1965 who measured $\text{Fe}_{1.67}\text{Ge}$ at 77K. He analyzed the spectrum assuming three different hyperfine fields, one for the 2(a) sites with the greatest intensity and the other two for the 2(d) sites with smaller intensity but

TABLE 1.1

Magnetic moments attributed to the 2(a) and 2(d) sites in
Bohr magnetons

		2(a)	2(d)
Kanematsu (12) experimental	n_f	0.8	2.8
	n_p	2.0	3.0
Kanematsu (13) theoretical		2.0	1.0
Katsuraki (10)		1.56 ± 0.10	0.53 ± 0.20
Forsythe and Brown (11)		1.4 ± 0.1	1.9 ± 0.1
Adelson and Austin (8)		1.30 ± 0.10	1.10 ± 0.10

larger hyperfine fields. The poor resolution did not permit determination of the quadrupole splitting of the component spectra. He could offer no clear explanation for the two hyperfine fields on the 2(d) sites.

Fatséas and Lecocq (16) were the next to publish a Mössbauer spectrum. They chose the composition $\text{Fe}_{1.5}\text{Ge}$. Unfortunately the low iron members of the series have even less well resolved component spectra than the higher iron content members, and the two component six-line spectra fit does not now appear realistic.

Next Germagnoli et al (17) published results on samples ranging from $\text{Fe}_{1.5}\text{Ge}$ to $\text{Fe}_{1.68}\text{Ge}$ in which they concentrated on the outside parts of the spectra from which they obtained two hyperfine fields. They did not attempt analysis of the whole spectrum.

Fatséas et al (18) show spectra for four samples over the composition range $\text{Fe}_{1.5}\text{Ge}$ to $\text{Fe}_{1.9}\text{Ge}$ measured at room temperature. The spectra were fitted assuming the hyperfine field to depend upon the number of iron neighbours near each site. The intensity of each component spectrum is obtained assuming a binomial distribution of atoms on the sites and consistent fits appear to be obtained to all four spectra. Finally Daniels et al (9) show spectra for five samples from $\text{Fe}_{1.58}\text{Ge}$ to $\text{Fe}_{1.99}\text{Ge}$ which they fit assuming three component spectra. They also report measurements with an applied field of 13.5K0e in the γ -ray direction with aligned absorbers so that the applied field is perpendicular to the crystallographic c-axis. They claim to observe canting angles of 90° for one of their three sites and they obtain very surprising changes in hyperfine field when they apply the magnetic field for which they offer no explanation.

1.6 Anisotropy measurements

Three investigators have reported anisotropy measurements.

Katsuraki (10) found that the c-axis was a hard magnetization direction from magnetic torque measurements. He was unable to observe any anisotropy in the basal plane. This result was corroborated by Tawara (19) who obtained a value of anisotropy constant:

$$-9 \times 10^6 \text{ erg. cm}^{-3}$$

Becker and Symes attempted to observe anisotropy in the basal plane by grinding a polycrystalline sample so that each particle was a small single crystal. These particles were then aligned in an applied magnetic field and the orientation was checked using x-ray diffraction. They do not however describe the x-ray diffraction results in detail but they estimate the basal plane anisotropy at 77°K as:

$$\geq 1.5 \times 10^4 \text{ erg. cm}^{-3}$$

1.7 Preliminary Conclusions

The following areas were identified in which further work would help to clarify the contradictory experimental position.

- i) It was suspected that some of the differences in results, for example Mössbauer spectra, arose from differences in the actual samples either from the affects of impurities or from slight differences in form resulting from different heat treatments. Consequently it was realized that the effects of different heat treatments should be investigated.

- ii) The temperature range over which Mössbauer measurements had been carried out was somewhat restricted and it was felt that there might be a temperature at which the component spectra were more easily resolved. It was therefore indicated that measurements should be carried out over as wide a range as possible from above the Curie temperature down to 4.2°K.
- iii) In such a complex structure it was thought that the statistics of published spectra were too poor to allow spurious fits to be ruled out and it was consequently considered worthwhile to prepare samples containing enriched iron.
- iv) It was considered that the application of a stronger magnetic field than had been available to other investigators would provide more information about the complex system and it was decided to make use of the available 50 kOe superconducting magnet.
- v) It was considered useful to have single crystals available both for checking magnetization results in view of the high uniaxial anisotropy and also for making Mössbauer absorbers with the crystallographic axes in known directions.

CHAPTER 2

SAMPLE PREPARATION

2.1 Method of Preparation

To prepare polychrystalline samples, stoichiometric amounts of iron sponge (99.999%) and germanium powder (99.999%) were weighed out. Reduction of the iron was carried out by heating to 700°C while maintaining a flow of hydrogen gas. The iron and germanium were then thoroughly mixed and pressed into a pellet using a hardened steel die. The pellet was placed in a vicor tube and filled with, typically, ≈ 100 mm Hg of Argon, so that at the temperature of the subsequent heat treatment the pressure would be ≈ 760 mm Hg. The tubes were then sealed off. Heat treatment was carried out in a 4.5 kW tube furnace manufactured by The Sentry Company, the temperature being controlled with a percentage time switch and measured using a Pt/Pt-10% Rh thermocouple and a Leeds and Northrup potentiometer. This enabled the temperature to be maintained to within $\pm 20^\circ\text{C}$ over a period of a few days.

For each composition two samples were made, one of mass ≈ 1 g containing natural iron (2% ^{57}Fe) and the other of mass ≈ 100 mg containing isotopically enriched iron (20% ^{57}Fe).

2.2 Heat Treatment

In the literature there is some variation in the heat treatments used. Some investigators carried out an initial heat treatment to ensure homogeneity. Adelson and Austin (8), for example, maintained their samples above the melting point for two days, whereas Yamamoto (15) sintered at 1000°C for two days. Fatséas et al (18) and Daniels et al (9),

on the other hand, carried out no initial heat treatment. Recently, Eliezer et al (20) performed Mössbauer measurements on mixtures of iron and germanium corresponding to $\text{Fe}_{1.7}\text{Ge}$, which had been sintered for times ranging from ten minutes to two hours at 600°C . It can be seen from their results that after two hours the reaction is 99% complete. It appears that the initial heat treatment is unnecessary and it is the final heat treatment that determines the properties of the sample. If a large sample is to be broken up into smaller parts, however, it is necessary to perform an initial heat treatment in order to ensure that each part will have the same composition.

From the phase diagram, it can be seen that $\text{Fe}_{1.95}\text{Ge}$ alloys must be quenched from 1100°C in order to preserve pure β -phase. For lower iron content, the samples may be cooled slowly. The lowest iron content alloys must not be annealed at temperatures greater than 1000°C . In the literature the annealing temperatures chosen are consistent with this, except that Daniels et al (9) prepared samples by cooling slowly from the melting point of iron. There have been reports that for $\text{Fe}_{1.95}\text{Ge}$ there is an unavoidable precipitate of α -iron when the alloy is quenched from 1100°C (7,17).

The heat treatment finally used was to maintain $\text{Fe}_{1.55}\text{Ge}$ samples at 900°C for three days and then to quench. $\text{Fe}_{1.70}\text{Ge}$ samples were maintained at 1070°C for 24 hours and quenched. The effects of several different heat treatments for $\text{Fe}_{1.95}\text{Ge}$ were investigated and the results are discussed later. Pure β -phase, however, was obtained by quenching as fast as possible from 1100°C .

2.3 Sample Purity

At each stage of preparation, the samples were weighed and the total loss for the 1 g samples was less than 10 mg or 1% whereas the 100 mg samples incurred losses of up to 5%. Subsequent comparison of the properties of corresponding 1 g and 100 mg samples showed, however, that any differences resulting from uncertainties in composition were negligible. Further determination of chemical composition was not attempted since the properties under investigation were not strongly composition dependent.

Powder diffractometer measurements were carried out on all samples. These were performed using a Philips diffractometer. 40 kV, Cu, K α radiation was used, using a Ni filter to remove the β -component. Scanning was carried out using a speed of $\frac{1}{2}^\circ$ per minute (for twice the Bragg angle). 'Rate-meter' method of data collection was used and the output was recorded on a paper chart. From the chart, angles and approximate intensities of the observed maxima could be obtained though no attempt was made to obtain accurate intensity measurements. From the line positions, values of lattice parameter were obtained using a computer fitting programme. The lattice parameters were in reasonable agreement with published data and are shown in figure 2.1. In addition no extra lines were observed, indicating that the samples were pure β -phase.

Unfortunately, α -iron has its main diffraction maxima close to the maxima in the β -phase, consequently x-ray diffraction is not very sensitive to small impurities of α -iron. However, the hyperfine fields are quite different and Mössbauer spectra can give reliable estimates of the amount of iron impurity. Furthermore, a two phase mixture, in which

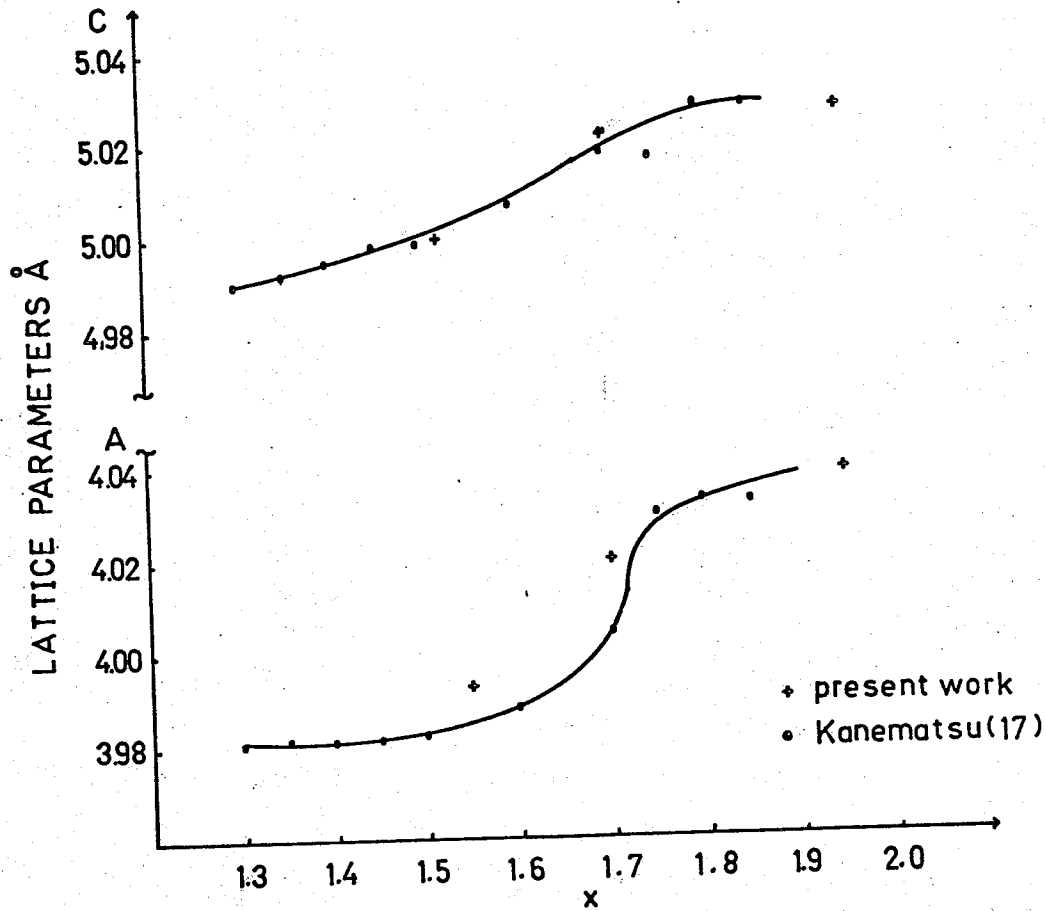


Fig. 2.1 Lattice parameters for the β -phase as a function of composition

the components have different Curie temperatures, may be shown to be a mixture by measuring between the two Curie temperatures, provided both impurities contain iron. These techniques were used to indicate impurities before the samples were considered acceptable.

2.4 The effect of cooling rate on $\text{Fe}_{1.95}\text{Ge}$

The crystalline forms of $\text{Fe}_{1.95}\text{Ge}$ at room temperature depends critically on the rate of cooling from the temperature at which it is stable (1100°C). The cooling rate can be characterized by the time τ which is the time taken for the difference between the original temperature and room temperature to reduce by one half. The following methods were used to obtain different values of τ :

(i) $\tau > 10^4$ sec.

Sample not removed from furnace. Furnace setting
slowly reduced.

(ii) $\tau \approx 10^3$ sec.

Sample not removed from furnace. Furnace switched off.

(iii) $\tau \approx 10$ sec.

Sample removed from furnace. Unbroken ampule
allowed to cool in air.

(iv) $\tau \approx 1$ sec.

Sample removed from furnace. Unbroken ampule
quenched in water.

(v) $\tau \approx 0.1$ sec.

Sample removed from furnace. Quenched by breaking
ampule under water.

The values of τ are only approximate and are based upon observation of the time taken for the sample to stop glowing. In each case the resulting material was investigated using both x-ray diffraction and Mössbauer effect.

Powder x-ray diffractometer results for angles from 41° to 48° are shown in figure 2.2. For $\tau \geq 10^3$ s. impurity lines coming from hexagonal ϵ -phase Fe_3Ge are clearly observable as would be expected from the phase diagram. For $\tau \approx 10$ s. similar results are obtained but some of the lines have somewhat changed shapes. For $\tau \approx 1$ s. there is apparently only β -phase present as no additional lines are observed but a slight broadening can be seen. $\tau \approx 0.1$ s. gave apparently a single phase with line shapes comparable with those obtained from $\text{Fe}_{1.70}\text{Ge}$.

The Mössbauer spectra for the same samples are shown in figure 2.3 and they show the origin of the impurity lines and the line broadening in the x-ray measurements. For $\tau \geq 10^3$ s. a six line component spectrum with hyperfine field of 240 kOe is observable which is equal to the hyperfine field measured for a sample known to be ϵ -phase Fe_3Ge .

For $\tau \approx 10$ s. the ϵ -phase component is still present but now there is another six-line component with a hyperfine field of 330 kOe. This corresponds to b.c.c. α -iron. The precipitate of α -iron for intermediate cooling rates observed in these Mössbauer spectra is in agreement with the results of Kanematsu (7) who observed a similar precipitate using magnetization measurements above the β -phase Curie temperature. The three phase system is meta-stable and is formed only because the iron precipitate has not had time to react fully with the

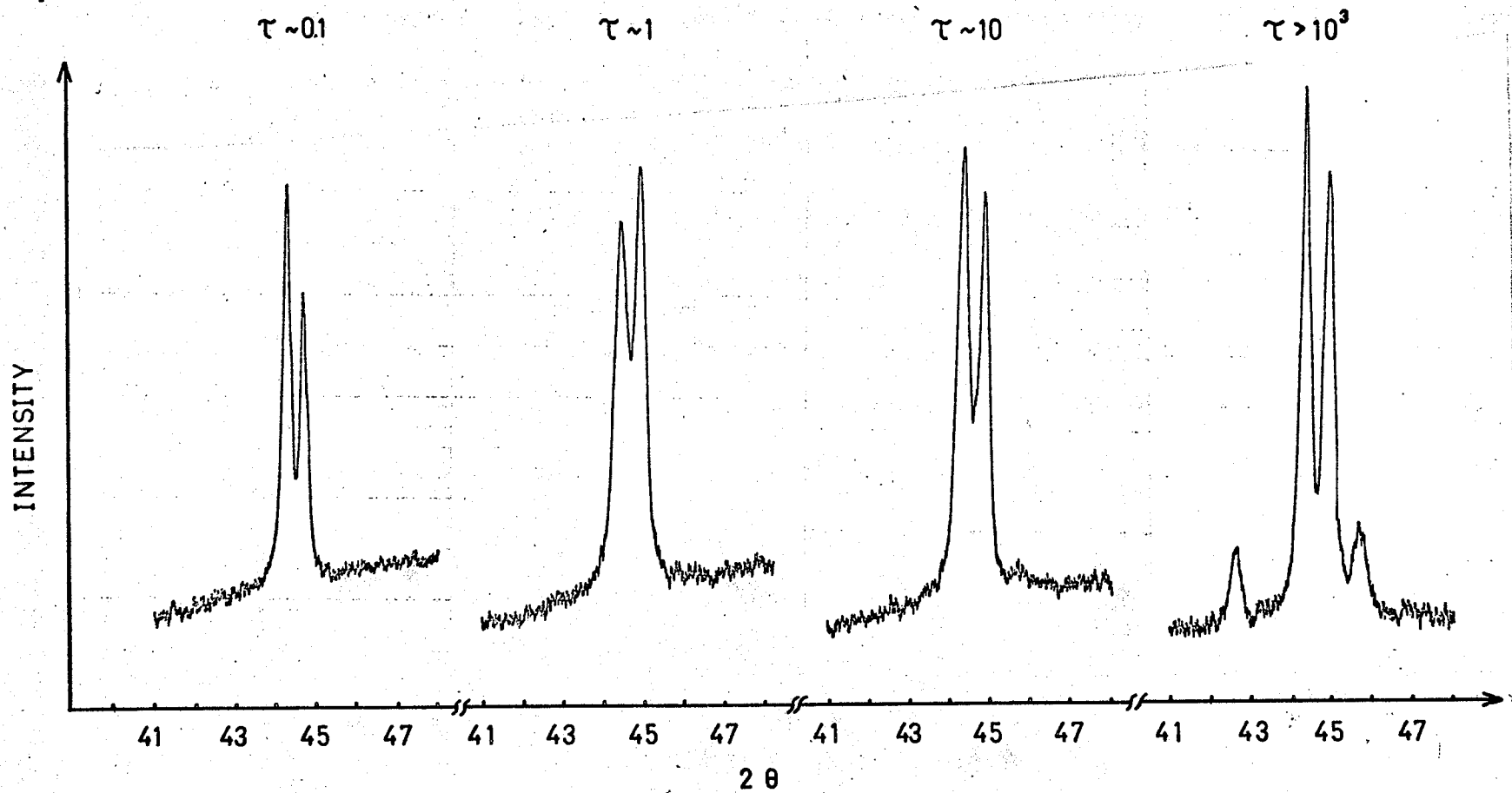


Fig. 2.2 The diffraction pattern of Fe_{1.95}Ge for various quench rates