THE DEFECT STRUCTURE OF $(Fe_{1-x}Co_x)_2$ RE COMPOUNDS (RE = Gd AND Tb)

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Constitutional investigations of Fe-RE, Co-RE and Fe-Co-RE systems revealed that it requires an "RE" content in excess of $(Fe_{1-x}Co_x)_2$ RE composition in order to prepare these compounds free from the presence of phases. A comparison of experimental and theoretical densities (calculated from the volumes of the unit cells) showed that the number of vacant TM (TM=Fe, Co or Fe+Co) sites vary from 7.5% for $(Fe_{0.32}Co_{0.68})_2$Gd to 2.5% in the binary Fe_2Gd compound. Likewise, there are 7.1% such sites in $(Fe_{0.33}Co_{0.67})_2$ Tb and 3.8% in the binary Co_2 Tb compound. Thus, it was concluded that the defects in the lattices of these compounds, responsible for the deviation from ideal stoichiometric compositions are vacancies on Fe and Co sites in respective binary compounds and on Fe+Co sites in ternary compounds.

Key words: Lattice defects, $(Fe,Co)_2$ RE Compounds.

Introduction

The compounds of terbium and gadolinium with Fe and Co having an A_2B type stoichiometry from through peritectic reactions as shown in the respective phase diagrams [1-4] (Figs. 1 and 2). These compounds crystallize in a cubic Cu_2Mg type structure [5-8]. Dwight and Kimball [9] however, reported a rhombohedrally distorted cubic structure for Fe_2Tb compound. They attributed this distortion to the huge "111" type room temperature magnetostriction which transforms the cubic lattice into rhombohedral, whereas all other researchers confirm a cubic structure [10-12].

When the Fe content of the Fe_2Tb and Fe_2Gd is gradually replaced by Co to form a range of $(Fe_{1-x}Co_x)_2$ Tb and $(Fe_{1-x}Co_x)_2$ Gd compounds, a complete range of solid solubility is observed for "x" ranging from zero to one, thus forming pseudo-binary systems as depicted by partial isothermal section of the Fe-Co-Tb [13] and Fe-Co-Gd [14] phase diagrams in Fig. 3(a,b).

Various Fe-RE and Co-RE (RE=rare earth) compounds show deviation from their ideal stoichiometric compositions [13,15]. This research was aimed at finding the defects in the lattices of these compounds, which cause deviation from stoichiometric composition. This work forms a part of a more extensive study of several Fe-Co-RE systems.

Experimental

Alloy preparation. A number of alloys, near the $(Fe_{1-x}Co_x)_2$ RE composition with varying $(Fe_{1-x}Co_x)$ content ("x" ranging from zero to one), were prepared for this investigation. The constituents (purities: Fe & Co = 99.99% and Tb & Gd = 99.9%) were melted in an argon arc furnace with a non-

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consumable tungsten electrode. Titanium gettered argon was used to prevent oxidation during melting hence the oxygen content of the alloys was negligable. Each alloy was remelted several times to ensure homogeneity and was subsequently analysed for its composition. Alloys which yielded single phase microstructures after homogenization, were chosen for this study whereas the rest were discarded. These alloys are listed in Table 1.

Heat treatment. Samples of each alloy were encapsulated in silica tubes, with a partial pressure of argon, for heat treatment. Alloys were homogenized at 1050±5° for two weeks and were subsequently quenched in iced brine (at about -15°) from the homogenization temperature.

Optical and scanning electron microscopy. Sample preparation for microscopy included cold mounting, dry grinding and polishing on progressively finer grades of diamond paste down to 0.25μ. Polished samples were etched with 2% nital for optical microscopy whereas a coating of carbon was

TABLE 1. COMPOSITION OF ALLOYS PREPARED FOR THIS
INVESTIGATION, AS DETERMINED BY ATOMIC
ABSORPTION SPECTROMETRY.

Alloy designation	Composition (%)			
	Fe	Co	Tb	Gd
T1	65.3	–	34.7	–
T2	43.6	21.3	35.1	–
T3	21.5	43.7	34.8	–
T4	–	65.6	34.4	–
G1	66.2	–	–	38.8
G2	44.1	21.0	–	34.9
G3	20.8	44.2	–	35.0
G4	–	ʻ66.1	–	33.9

applied to the polished samples for scanning electron micro-scop (SEM).

X-Ray diffraction. X-ray diffraction was carried out on powder samples of homogenized alloys. Homogenized bulk samples were crushed and ground to make fine powder in an agate mortar. Powder samples of a few alloys were annealed at 600-650° to check the effects of strains, induced during grinding of the alloys, on the lattice spacings. A negligible

difference was observed in the lattice spacings of annealed and non-annealed powder samples, which was within the accuracy limits of the equipment. X-ray work was carried out on a Philips PW1710 diffractometer equipped with a monochromator and employing Cu-Kα radiation with an average weighted wavelength of 1.54178°. Diffraction patterns were analysed using the Nelson-Riley extrapolation [16] method for elimination of systematic errors. Volumes of the unit cells were calculated from the lattice constants of various compounds for subsequent determination of theoretical densities.

Determination of Densities.

(a) Theoretical density. The theoretical density of a compound is given by:

Density = Mass of unit cell/volume of unit cell............1

The volumes of unit cells were calculated using the lattice constants and masses from the number of atoms of different elements in the unit cells. The unit cell of TM_2RE type compounds (TM=Fe, Co or Fe+Co) correspond to eight formula unit cell and thus comprise of eight "RE" atoms and sixteen "TM" atoms. The masses of atoms of the various
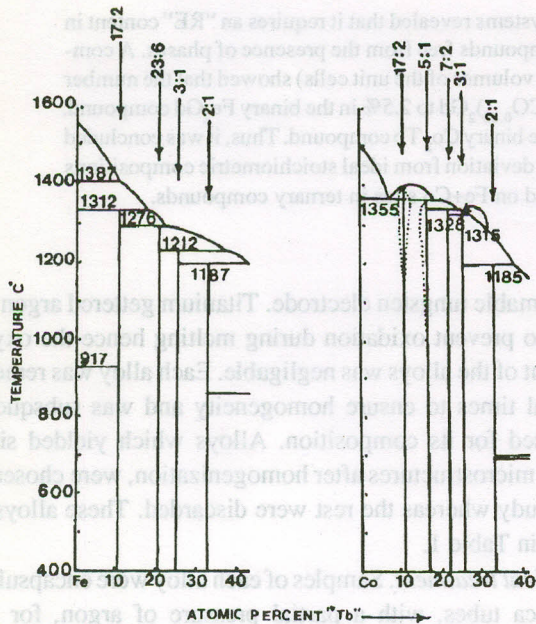

Fig. 1. Fe and Co rich ends of Fe-Tb and Co-Tb phase diagrams (redrawn from reference 1 and 2).
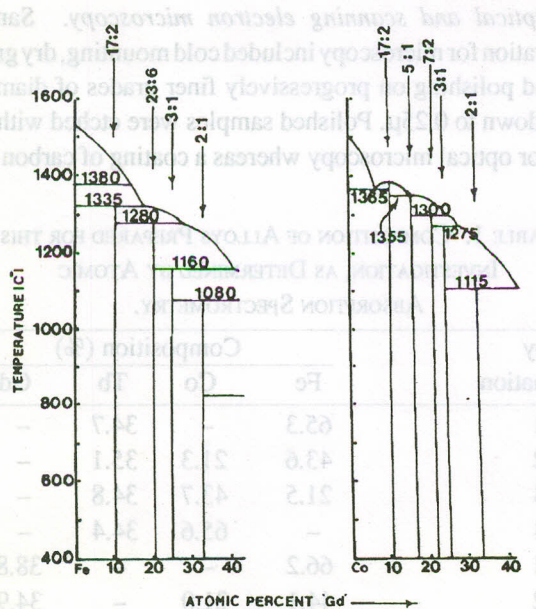

Fig. 2.Fe and Co rich ends of Fe-Gd and Co-Gd phase diagrams (redrawn from references 3 and 4).

TABLE 2. Lattice Constants and Volumes of Unit Cells of Various $(Fe_{1-x}Co_x)_2Tb$ and $(Fe_{1-x}Co_x)_2Gd$ Compounds (for "x" Ranging from Zero to One).

Alloy designation	Compounds	Lattice constant 'A'(°A)	Volume of unit cell $(10^{-23} cm^3)$
T1	Fe_2Tb	7.9706	5.0637
T2	$(Fe_{0.67}Co_{0.33})_2Tb$	7.9482	5.0212
T3	$(Fe_{0.33}Co_{0.67})_2Tb$	7.8996	4.9296
T4	Co_2Tb	7.8344	4.8085
G1	Fe_2Gd	7.3895	4.0350
G2	$(Fe_{0.68}Co_{0.32})_2Gd$	7.3656	3.9959
G3	$(Fe_{0.32}Co_{0.68})_2Gd$	7.3173	3.9179
G4	Co_2Gd	7.2564	3.8209

TABLE 3. Compositional Analyses of $(Fe_{1-x}Co_x)_2$ RE Compounds (for "x" Ranging from Zero to One), as Determined by EDX Analysis.

Alloy designation	Composition (%)				TM:RE
	Fe	Co	Tb	Gd	
T1	65.2	–	34.8	–	2:1.07
T2	43.8	21.2	35.0	–	2:1.08
T3	21.4	43.8	34.8	–	2:1.07
T4	–	65.8	34.2	–	2:1.05
G1	66.2	–	–	33.8	2:1.02
G2	44.0	21.1	–	34.9	2:1.07
G3	20.8	44.1	–	35.1	2:1.08
G4	–	66.1	–	33.9	2:1.03

Table 4. Theoretical Densities for Various Defect Mechanisms of $(Fe_{1-x} Co_x)_2$ RE Compounds Along with Experimental Data.

Alloy	Stoichiometric formula*	Theoretical density for defect free unit (g/cm³)	Theoretical density for various defects in the lattices (g/cm³)			Experimentally measured densities (g/cm³)	Percentage of vacant "TM" sites
			'A'	'B'	'C'		
T1	$Fe_2 Tb$	7.09	7.38	7.20	6.91	6.95	6.3
T2	$(Fe_{0.67} Co_{0.33})_2 Tb$	7.16	7.48	7.29	6.95	6.97	7.1
T3	$(Fe_{0.33} Co_{0.67})_2 Tb$	7.29	7.57	7.42	7.10	7.04	6.3
T4	$Co_2 Tb$	7.48	7.65	7.55	7.36	7.16	3.8
G1	$Fe_2 Gd$	8.85	8.96	8.90	8.77	8.78	2.5
G2	$(Fe_{2.68} Co_{0.32})_2 Gd$	8.94	9.32	9.10	8.69	8.70	6.7
G3	$(Fe_{0.32} Co_{0.68})_2 Gd$	9.12	9.55	9.31	8.83	8.79	7.5
G4	$(Co_2 Gd$	9.35	9.35	9.42	9.26	9.18	2.5

A = Rare earth atoms occupying interstitial sites, B = Rare earth atoms substituting for Fe, Co or Fe+Co atoms, C = Vacancies at Fe, Co or Fe+Co sites, * = For experimentally determined formula see Table 3.

elements, as calculated by employing Avogadro's law are as follows:

Fe = $9.2730286 \times 10^{-23}$ g
Co = $9.2873083 \times 10^{-23}$ g
Tb = $2.6388289 \times 10^{-22}$ g
Gd = $2.6110333 \times 10^{-22}$ g

(b) Experimental density. Archimedes principle was adopted to evaluate the densities of the various compounds. The density is given by the following relation:

$$d = (Wa.dw - Ww.da) / (Wa-Ww) \dots\dots\dots\dots (2)$$

where d = Density of the sample, Wa = Mass of sample in air, dw = Density of water at room temperature, Ww = Mass of sample in water, da = Density of air at room temperature

The bulk samples were weighed both in air and in water to an accuracy of 0.001mg. Three measurements were made on each sample and an average value was used the calculations.

Results and Discussion

The microstructural examination of the as-cast samples of all the alloys revealed a microstructure consisting of three phases, which is typical of the compounds formed peritectically. Homogenization of these alloys however, resulted in microstructures, composed of Tm_2RE compounds, free from other phases as demonstrated by micrographs in Fig. 4.

X-Ray diffraction patterns of the homogenized samples showed reflections corresponding only to TM_2RE compounds. However, in alloys T_3 and G_2, few very weak reflections were observed which did not correspond to TM_2RE compounds. The relative intensity of these unidentified reflections were negligible as compared to the diffraction lines for matrix phase namely, the TM_2RE compounds, so it was reasonable to assume that even if second phases were present in the alloys, their volume fraction was negligible as compared to the matrix
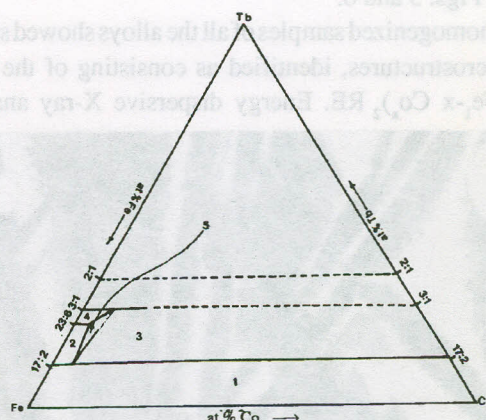

Fig. 3(a) Partial isothermal section of Fe-Co-Tb phase diagram at 1050° (redrawn from reference 13). The phase fields are given as the ratios of Fe+Co to Tb:

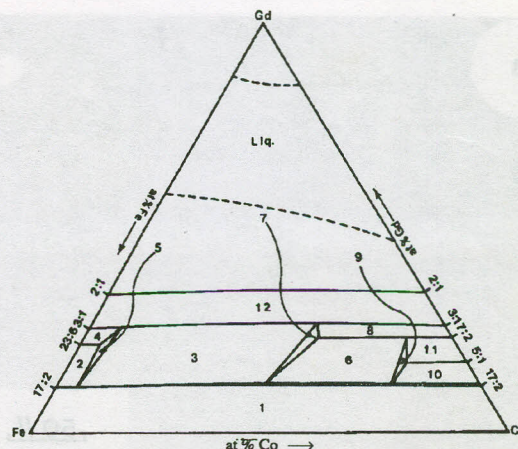(1) 17:2 + Fe-Co solid solution (2) 17:2 + 23:6 (3) 17:2 + 3:1 (4) 23:6 + 3:1 (5) 17:2 + 23:6 + 3:1 (6) 3:1 + 2:1

Fig. 3(b) Partial isothermal section of Fe-Co-Gd phase diagram of 1050° (redrawn from reference 14). The phase fields are given as the ratios of Fe+Co to Gd:

(1) 17:2 + Fe-Co solid solution (2) 17:2 + 23:6 (3) 17:2 + 3:1 (4) 23:6 + 3:1 (5) 17:2 + 23:6 + 3:1 (6) 17:2 + 7:2 (7) 17:2 + 7:2 + 3:1 (8) 7:2 + 3:1 (9) 17:2 + 5:1 + 7:2 (10) 17:2 + 5:1 (11) 5:1 + 7:2 (12) 3:1 + 2:1.

(TM$_2$RE) compound.

It was possible to obtain values of lattice constants to an accuracy of 0.0004° A by employing the Nelson Riley extrapolation procedure to eliminate the systematic error. Table 2 summarizes the values of lattice constants for the various (Fe$_{1-x}$ Co$_x$)$_2$RE (RE = Tb & Gd) compounds for "x" ranging from zero to one. The lattice constants of both the (Fe$_{1-x}$ Co$_x$)$_2$ Tb and the (Fe$_{1-x}$ Co$_x$)$_2$ Gd compounds show a progressive decrease as a function of "x" (Figs. 5 and 6).

This can be attributed to the increasing number of cobalt atoms (which have smaller atomic radii) replacing Fe atoms as the value of "x" increases in the compound. The volumes of the unit cells as calculated from the lattice constants (Table 2) also demonstrate a progressive decrease as a function of "x" as shown in Figs. 5 and 6.

The homogenized samples of all the alloys showed single-phase microstructures, identified as consisting of the compound (Fe$_{1-x}$ Co$_x$)$_2$ RE. Energy dispersive X-ray analyses

demonstrated that all the compounds show a definite deviation from the ideal stoichiometric compositions. The deviation, although not constant, was in all the cases towards a higher "RE" concentration. The analyses of the various compounds are given in Table 3. The deviation from ideal stoichiometric composition can be attributed to one of the following defect mechanisms:

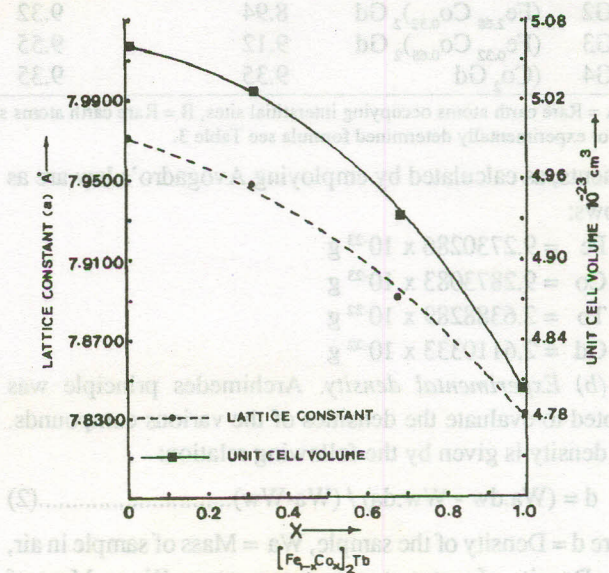(i)   Vacancies on Fe or Co sites in the binary compounds and on Fe+Co sites in the ternary compounds.

Fig. 5. Variation in the lattice constants and volumes of unit cells as a function of "x" in (Fe$_{1-x}$ Co$_x$)$_2$ Tb compounds.

Fig. 6.   Variation in the lattice constants and volumes of unit cells as a function of "x" in (Fe$_{1-x}$Co$_x$)$_2$ Gd compounds.

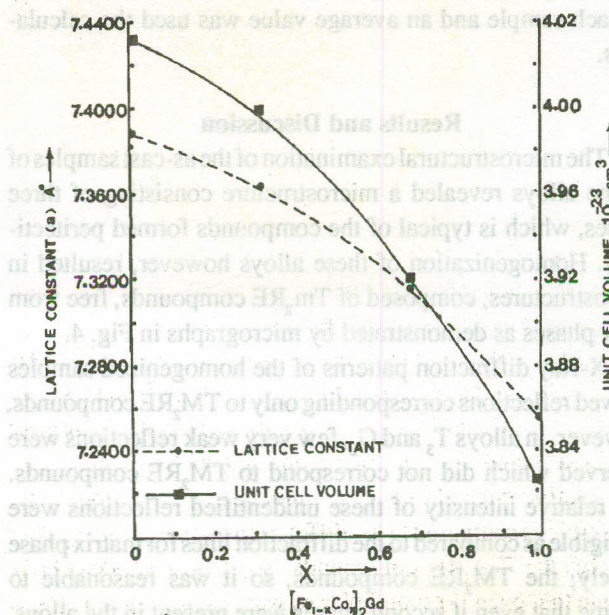Fig. 4. Scanning electron micrographs of alloy G$_2$ in back scattered electron imaging (BEI) mode.

(A) The as-cast microstructure showing (Fe, Co)$_{17}$Gd$_2$ (dark), (Fe, Co)$_3$Gd (grey) and (Fe,Co)$_2$Gd (bright) phases.

(B) The homogenized microstructure showing only one phase i.e., (Fe,Co)$_2$ Gd compound.

(ii) RE atoms (Tb or Gd) occupying interstitial sites in the unit cells of the respective compounds.

(iii) RE atoms (Tb or Gd) substituting for Fe or Co atoms in the respective binary compounds and Fe+Co atoms in the ternary compounds.

Densities for the various $(Fe_{1-x}Co_x)_2$ RE compounds were calculated considering all of the above mentioned possibilities for defects in the lattices. The density values based on the assumption that the defects in the lattices were vacancies,
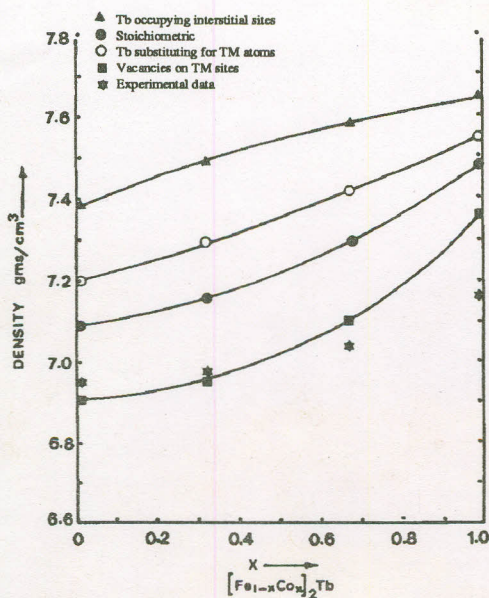

Fig. 7. Comparison of theoretical densities of $(Fe_{1-x}Co_x)_2$ Tb compounds (for various defects mechanisms) with the experimental data, plotted as a function of "x".
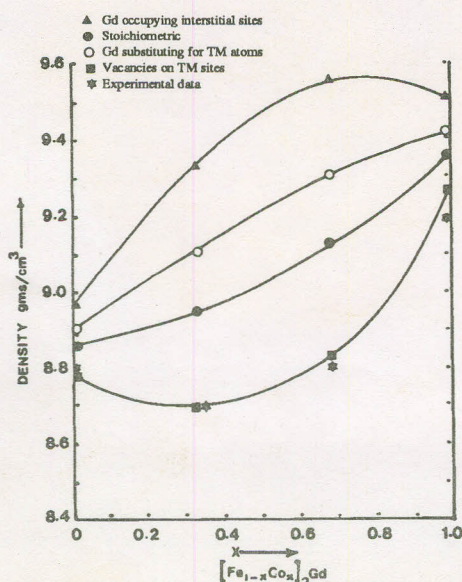
Fig. 8. Comparison of theoretical densities of $(Fe_{1-x}Co_x)_2$ Gd compounds (for various defects mechanisms) with the experimental data, plotted as a function of "x".

were considerably lower than the other two assumptions for defects, namely, the interstitial and substitutional defects. The data thus obtained were plotted as a function of "x" for the $(Fe_{1-x}Co_x)_2$ Tb and $(Fe_{1-x}Co_x)_2$ Gd compounds as shown in Figs. 7 and 8. The experimentally measured densities, along with theoretical densities, are given in Table 4.

A comparison of the densities based on different possibilities of defects in the lattices with the experimentally measured densities shows that the experimental data lie very close to the curve for the vacancy model of defects. This implies that the defects in the lattices of $(Fe_{1-x}Co_x)_2$ Tb and $(Fe_{1-x}Co_x)_2$ Gd type of compounds are vacancies on Fe, Co or Fe+Co sites. This conclusion is supported by the fact that the atoms of Tb and Gd which have larger atomic size (1.80° A and 1.79° A respectively) as compared to Fe or Co (1.26 and 1.25° A respectively), would cause substantial distortions in the lattices if these were to occupy interstitial sites or to substitute for Fe or Co atoms.

The number of vacant "TM" sites was also calculated for each compounds and the percentage of vacant "TM" sites is summarized in Table 4.

Conclusions

From the above discussion, the following conclusions can be made:

The cause of deviation from stoichiometric composition towards a higher "RE" content in the $(Fe_{1-x}Co_x)_2$ Tb and $(Fe_{1-x}Co_x)_2$ Gd compounds is the presence of vacancies on Fe or Co sites in the respective binary compounds and on Fe+Co sites in the ternary compounds.

The number of vacant "TM" sites vary as a function of "x" in the compounds. This variation however, does not follow any simple relationship.

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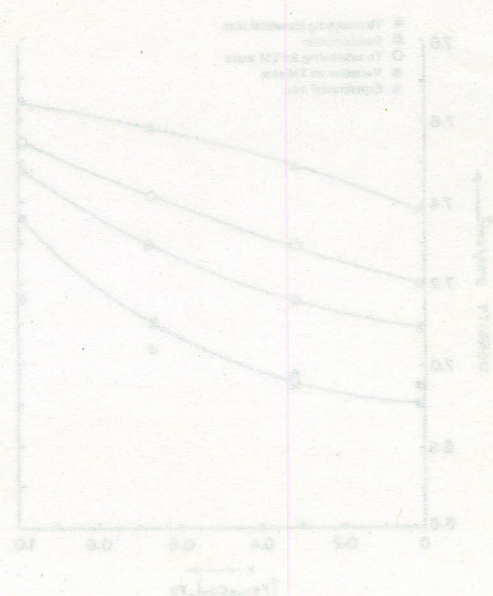8. K.H.J. Buschow and A.S. Van Der Goot, Journal of the Less Common Metals, **17**, 249 (1969).

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