Lavesphase pseudobinaries A(Fe1x B x)2 (A=Zr, Hf; B=Al, Si): Some structural and magnetic properties

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Laves-phase pseudobinaries $A(Fe_{1-x}B_x)_2$ (A=Zr, Hf; B=Al, Si): Some structural and magnetic properties

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The lattice parameters and the saturation magnetization are measured for the series of intermetallic compounds $A(Fe,B)_2$, A = Zr, Hf and B = Si and Al, with concentrations less than 15%. The magnetization measurements and the lattice parameter behavior are qualitatively discussed.

I. INTRODUCTION

Laves-phase compounds are well known for the possibility of selectively dissolved impurities in the A or in the B sublattices. Structurally $ZrFe_2$ is a single-phase, cubic $C15$ intermetallic, whereas $HfFe_2$ exhibits the coexistence of $C15$ and hexagonal $C14$ phases.[1] It was experimentally shown that adequate concentrations of Si impurities substituted for Fe, stabilize a pure $C15$ phase in $HfFe_2$ intermetallics.[1] Magnetization studies have been performed in pseudobinaries of Zr with Al replacing Fe, suggesting that site dilution effects are introduced by these impurities.[2]

In this work we have measured the lattice parameters for the single-phase pseudobinaries, identified the amount of the $C15$ and $C14$ phases in $Hf(Fe,Si)_2$, and obtained the saturation magnetization in a series of compounds of Zr or Hf with Al or Si impurities replacing iron. Finally, we discuss qualitatively the magnetization data and suggest a simple interpretation of the lattice parameter changes.

II. EXPERIMENT

The samples were prepared in an arc furnace under argon atmosphere, and the range of concentration was chosen for both Si and Al from $x = 0.0$ to 0.15. Table I summarizes the results obtained for the crystal structure. It is clear from Table I that Si is capable of stabilizing, in an appreciable range of concentrations, the pure cubic phase for Hf intermetallics, in contrast to the Al impurities.

X-ray step-scan measurements were performed with ten steps per degree and 4000 counts per point. The diffractograms were fitted using a least-squares fitting code.

Magnetization measurements were performed in a homemade extraction magnetometer at room temperature and the maximum applied magnetic field was 8 kOe.

III. RESULTS FOR SINGLE-PHASE $C15$ COMPOUNDS

A. Structure and magnetic properties

Here we focus our attention on the Zr compounds (with Al or Si) and on the Hf compounds (with Si) that present the single cubic phase, and more specifically on the concentration range $0.03 < x < 0.13$.

In Fig. 1, the behavior of the cubic lattice parameter a^c is shown as a function of the concentration of Si and Al. We observe that a^c increases with Al concentration; Si however, decreases it for both compounds. This behavior opens the question of understanding why neighboring impurities in the periodic table induce such different behavior in the lattice parameter. The results of the saturation magnetization measurements are shown in Fig. 2. In the case of Zr pseudobinaries one sees that both *sp* impurities induce mainly site dilution like effects, characterized by a monotonic decrease of the magnetization with increasing concentration. For both impurities and for concentrations up to 0.10 quite similar effects on the saturation magnetization are observed. For $0.10 < x < 0.13$, however, the effect of Al impurities is slightly stronger. This behavior is to be contrasted with the quite different effects of Si and Al on the lattice parameters.

IV. RESULTS FOR THE $0 < x < 0.03$ REGION OF PHASE COEXISTENCE IN Hf COMPOUNDS

Consider Hf pseudobinaries with Si concentrations lower than 0.03; as indicated in Table I a mixed phase exists. In order to estimate the amounts of mixed phases we used the x-ray step-scan technique, together with the hypothesis of identical Si concentration in both phases. The chosen angular window was from $2\theta = 20°$ to 25°. In this angular interval the spectrum shows three lines of the hexagonal phase and one line to the cubic phase.[1] We carefully verified that the total diffracted energy in this angular region (area under the single peak of $C15$ or under the three peaks of the $C14$) is the same for both pure phases. For the study of coexisting phases we took samples $x = 0.0$, 0.005, 0.01, 0.025, since for $x = 0.03$ only the pure $C15$ phase exists. The amount of cubic phase α^{C15} was thus obtained from the ratio of the fitted areas through the formula

$$\alpha^{C15} = C/(C + H), \tag{1}$$

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TABLE I. Concentration dependence of the stability of the phases $C14$ and $C15$.

Compound	Mixed: $C14$ and $C15$	Pure: $C15$	Pure: $C14$
$Zr(Fe,Al)_2$	···	$0 \leq x \leq 0.20$	···
$Zr(Fe,Si)_2$	···	$0 \leq x \leq 0.17$	$0.17 < x \leq 0.20$
$Hf(Fe,Al)_2$	$0 \leq x \leq 0.13$	···	$0.13 < x \leq 0.20$
$Hf(Fe,Si)_2$	$0 \leq x < 0.03$	$0.03 < x < 0.13$	$0.13 < x \leq 0.20$

C and H being the areas corresponding to the cubic and hexagonal phases. The results are shown in Fig. 3. This is consistent with the decreasing amount of the $C14$ phase for increasing Si concentration, to finally arrive at the pure $C15$ phase for $x = 0.03$.

V. DISCUSSION

A. Magnetization data

The interpretation of the saturation magnetization data as a function of the impurity concentration involves the following aspects: the crystal structure and the $4d$ or $5d$ character of the A atom that modifies the $3d$ electronic structure at the B sites.

Since both impurities have sp character, one expects a strongly repulsive potential acting on d electrons, together with impurity-induced local d-p hybridization.[3] In this recent simplified calculation, using a model density of states, it was possible to show that both sp impurities induce a decreasing average magnetization as a function of concentration.

In Fig. 2 the arrows indicate the Si concentration range in which the pure $C15$ phase is simultaneously stable for Hf and Zr compounds. The saturation magnetization curves in this concentration range are approximately parallel, with lower magnetization values for the Hf compounds. Since the same crystal structure is present in both cases, the only difference is the $4d$ or $5d$ character of the A atoms. As previously suggested,[4] in this case one expects to have a charge transfer from A to B sites. Besides these pure charge-transfer effects, modifications of the local $3d$ density of states may also exist.

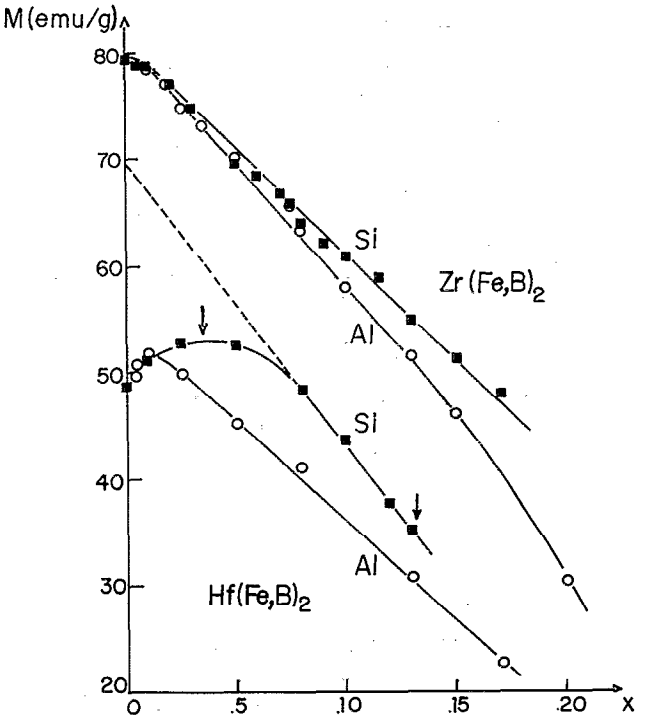

FIG. 2. Saturation magnetization for intermetallics with Si (filled squares) and Al (open circles).

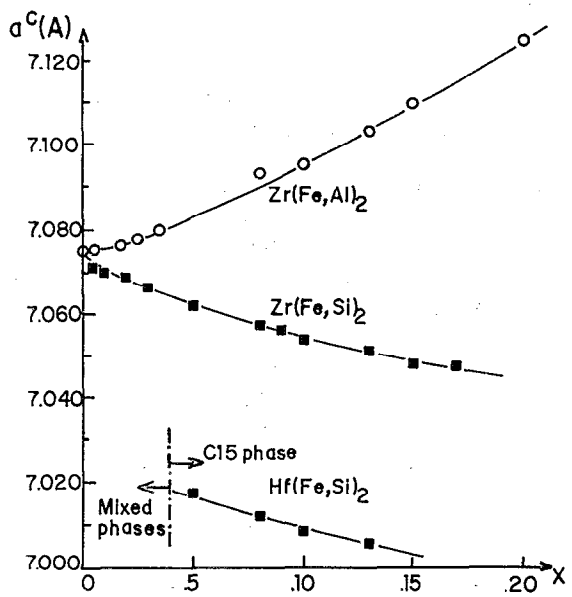

FIG. 1. Cubic-phase lattice parameters as a function of sp impurity concentration x. The full lines are guides to the eye.

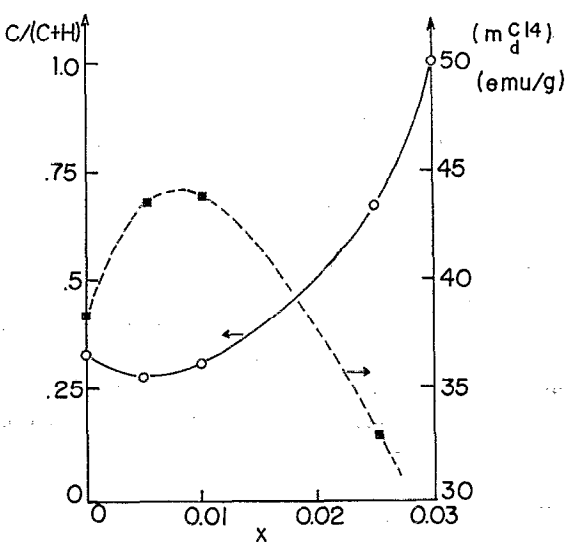

FIG. 3. Amount of $C15$ phase in $Hf(Fe,Si)_2$ intermetallics for $x \leq 0.03$ (open circles); magnetization of $C14$ phase as a function of Si concentration (filled squares).

The saturation magnetization for the $C15$ phase of $HfFe_2$ can be estimated from the extrapolation indicated in Fig. 2, using the simple dilution hypothesis. Thus the difference in magnetization between the $C15$ $HfFe_2$ and $ZrFe_2$ can be understood if one assumes that the density of states decreases with energy around the Fermi level. These combined effects, charge transfer and the site dilution associated with Si impurities, roughly explain the saturation magnetization data for this concentration region.

Consider now the Hf pseudobinaries with Si in the mixed phase. Using the results for α^{C15} obtained from the step-scan experiment it is possible to make a rough estimate of the magnetic moment of the $C14$ phase as a function of the concentration. Let us start from the measured saturation magnetization as a function of x shown in Fig. 2, and write

$$m_{\rm obs}^{\rm Hf(Fe,Si)}(x)=\alpha^{C15}(x)m_d^{C15\ (\rm extrap)}(x) + [1-\alpha^{C15}(x)]m_d^{C14}(x), \qquad (2)$$

where $m_d^{C15\ (\rm extrap)}(x)$ is the best straight line (site dilution effect) one can draw through the magnetic data in the pure $C15$ concentration region (Fig. 2). Using Eq. (2) the magnetization $m_d^{C14}(x)$ can be extracted and the result is shown in Fig. 3.

B. Lattice parameter variation

The concept of electronic pressure[5] is a very useful tool to understand the lattice parameter behavior. The electronic pressure is expressed in terms of the s, p, and d electron contributions through states in the sphere with $l=s$, p, and d, and the l-projected densities of states $\rho_l(\epsilon)$.[5] In the derivation of the expression for the pressure, the metals or intermetallics are assumed to be pure. In general, the electronic pressure as a function of the lattice parameter (Wigner–Seitz radius) is the result of a detailed competition of different sign contributions. Usually,[6] d states contribute with negative values, in contrast to the s and p electronic pressure. The equilibrium lattice parameter is determined from the zero of the total pressure.

In light of some of the above-reported experimental results, we suggest a simplified interpretation of the lattice parameter behavior. First of all, remember that, except in the case of phase coexistence, Al and Si produce identical modifications of the saturation magnetization. This fact suggests that Si and Al almost identically modify the d contributions to the pressure; the observed changes are then associated with the p and s electrons. It is tempting to assume that the s contribution is identical for both impurities. Consequently, through the changes in the p-projected densities of states, p occupation numbers, and different p states in the sphere, one can induce different changes in the equilibrium lattice parameters for Al and Si. Again, let us emphasize that this interpretation is based on the subtle compensations between the different contributions to the pressure. Recent first-principles calculations[7] have shown that impurity neighbors in the periodic table induce opposite charge transfers; this result provides another indication of the validity of our simple picture.

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