Full length article

On the characterisation of antisite defects and ordering in off-stoichiometric Fe$_2$VAl-based Heusler compounds by X-ray anomalous diffraction

Camille van der Rest [a], Alain Schmitz [b], Pascal J. Jacques [a, *]

[a] *Université catholique de Louvain (UCL), Institute of Mechanics, Materials and Civil Engineering, IMAP, Place Sainte Barbe 2 Bte L5.02.02, 1348 Louvain-la-Neuve, Belgium*
[b] *CRM Group, Avenue Du Bois Saint-Jean 21, B27–Quartier Polytech 4, 4000 Liège, Belgium*

ABSTRACT

Compounds based on Fe$_2$VAl are good candidates for low grade heat harvesting owing to the thermoelectric effect. However, it is claimed that their thermoelectric properties are badly influenced by antisite defects, especially at higher temperatures. The present study investigates order-disorder transitions in Fe$_2$VAl ternary Heusler compounds. An inherent problem of these compounds is the close atomic numbers of Fe and V, leading to similar x-ray atomic scattering factors. Hence, the D0$_3$ and L2$_1$ structures, corresponding to Fe-V antisite defects, are hardly distinguishable by X-ray diffraction. In this work, anomalous scattering and neutron diffraction were successfully combined with differential scanning calorimetry to highlight the order-disorder transitions in Fe$_2$VAl-based compounds. A model has been developed to quantify the ordering parameters. From these results, specific heat-treatments were defined to promote the formation of the L2$_1$ ordered phase.

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1. Introduction and background

Heusler alloys are the topic of numerous recent studies due to promising functional properties in various fields [1–3]. This is also the case for the Fe$_2$VAl compound that was shown to exhibit very interesting thermoelectric properties adequate for low grade heat harvesting [4–8]. Like other Heusler compounds of general formula X$_2$YZ (where X and Y are transition metals and Z is a main group element), the Fe$_2$VAl-based compound belongs to the cubic space group (Fm-3m) with four interpenetrating FCC sublattices. In a fully ordered configuration, two of these sublattices are occupied by X atoms, and the two other ones are occupied by Y and Z atoms, respectively. X atoms (Fe in the present case) occupy tetrahedral sites referred to as the 8(c) Wyckoff positions, while the Y and Z atoms (V and Al) occupy the octahedral 4(a) and 4(b) Wyckoff positions [1]. The resulting structure is the fully ordered Heusler structure, referred to as the L2$_1$ crystal structure and shown on Fig. 1. Perfect L2$_1$ order could be only partially present depending on the processing conditions. The crystal structure is then described more adequately using lower-ordered structures. If the V and Al atoms are randomly distributed, the 4(a) and 4(b) Wyckoff sites become equivalent, bringing B2-type disorder. As a consequence, the symmetry is reduced and the space group becomes Pm-3m [1]. If, on the other hand, V and Fe atoms interchange such that their distribution over the 8(c) and 4(a) sites is random, D0$_3$-type disorder is observed. It may be noted that this is the crystal structure of Fe$_3$Al (same space group Fm-3m). Finally, the A2-type structure arises in the case of completely random distribution of atoms. This disordered structure results in a BCC lattice which belongs to the Im-3m space group.

Bilc et al. [9] have shown that Fe-V antisite defects are the most detrimental antisite defects for the thermoelectric properties of Fe$_2$VAl-based compounds. It emphasises the importance of accurately characterising the degree of order of such Heusler compounds.

Powder X-ray diffraction (XRD) has been commonly used as experimental method to determine the crystal structure of Heusler samples [1,10]. The presence of the (111) superlattice reflection is sometimes considered in the literature as an evidence for the L2$_1$ structure [7]. Other authors calculate intensity ratios to identify the L2$_1$ structure, without making a clear distinction with the D0$_3$ phase [11,12]. However, it is recognised that powder X-ray
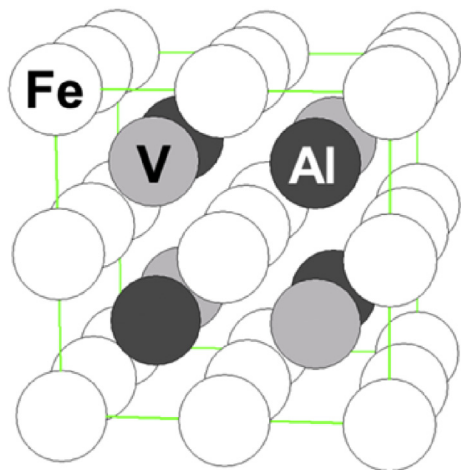
Fig. 1. Visualisation of the fully ordered $L2_1$ structure, so-called Heusler structure.

diffraction presents difficulties in discriminating some structures and identifying antisite disorder between elements with close atomic numbers, such as Fe and V [10]. Indeed, the X-ray diffracted intensities are proportional to the atomic numbers of the constitutive elements when X-ray source wavelength does not induce sample fluorescence (normal scattering). To overcome this drawback, anomalous XRD analysis could be helpful to properly determine the structure [1,13,14].

In XRD, the structure factor F_{hkl} characterises the wave diffracted by the different atoms of the unit cell for a (hkl) reflection and is used, among other factors (multiplicity, Lorentz-polarisation, temperature, and absorption), to determine the diffracted intensities [13,15]. Equation (1) shows the general expression of the diffracted intensity in XRD relating the diffracted intensity I_{hkl} to $|F_{hkl}|^2$, which is calculated by multiplying F_{hkl} by its complex conjugate [16]. In Equation (1), p_{hkl} is the multiplicity factor; LP factor is the Lorentz-polarisation factor resulting from geometrical considerations and from the fact that the incident beam is unpolarised; T factor is the temperature factor that takes into account thermal vibrations of the atoms[1] [15,17]. The absorption factor is independent of θ in the present configuration so that it does not influence relative intensities.

$$I_{hkl} \propto |F_{hkl}|^2 \cdot p_{hkl} \cdot \underbrace{\left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)}_{\text{LP factor}} \cdot \underbrace{exp\left(-2B\left(\frac{\sin \theta}{\lambda} \right)^2 \right)}_{\text{T factor}} \quad (1)$$

The structure factor F_{hkl}, for a (hkl) reflection and for a unit cell containing N atoms, is calculated as a function of the atomic scattering factors $f_1, ..., f_N$ by Equation (2) [13,16]. The structure factors are thus dependent on the position (u_n, v_n, w_n are the atomic coordinates) and nature of the atoms in the unit cell, hence on (dis)order.

$$F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)} \quad (2)$$

The normal atomic scattering factors $f_{at} = f_0$ are commonly used when no fluorescence is taking place. These ones are nearly

proportional to the atomic number Z_{at}, hence very similar for atoms like Fe and V. In the case of fluorescence, correction factors have to be added to describe more accurately the scattering of atoms. Equation (3) shows that the atomic scattering factors do include a complex energy-dependent contribution, f' + if'', referred to as the anomalous correction factors [13]. In this equation, f_0 is the normal contribution dependent on the centrosymmetry of the electron distribution and decreasing rapidly when increasing $\sin\theta/\lambda$, θ referring to the direction of observation and λ to the wavelength of the incident radiation.

$$f(\lambda, \theta) = f_0 \left(\frac{\sin \theta}{\lambda} \right) + f'(\lambda) + i f''(\lambda) \quad (3)$$

The anomalous contributions are most of the time insignificant in comparison to f_0, except in the vicinity of an absorption edge when core electrons can be excited by incident photons [13,17]. Fig. 2 shows, for Fe and V, the strong dependence of the anomalous contributions f' and f'' on energy, with large variations near absorption edges (5.4651 keV for V and 7.112 keV for Fe) [18]. By choosing incident X-ray with energy near the Fe or V absorption edges, the atomic scattering factors of these two atoms can be much more different so that it would be possible to identify with a larger contrast their positions in the lattice (and thus potentially Fe-V antisite disorder) [13].

2. Model for the identification and quantification of disorder in Fe₂VAl

2.1. Previous models

Takamura et al. suggested a model, based on anomalous XRD, which evaluates three disordering parameters (α, β, and γ) to characterise ordering in the Co_2FeSi Heusler compound [10]. Three types of antisite exchanges are considered: Fe/Si, Co/Si, and Co/Fe exchanges, whose numbers per unit formula correspond to the three disordering parameters, respectively. From experimental values of $|F_{111}|^2/|F_{220}|^2$ and $|F_{200}|^2/|F_{220}|^2$, obtained from XRD with Co and Cu sources, i.e. with different levels of anomalous
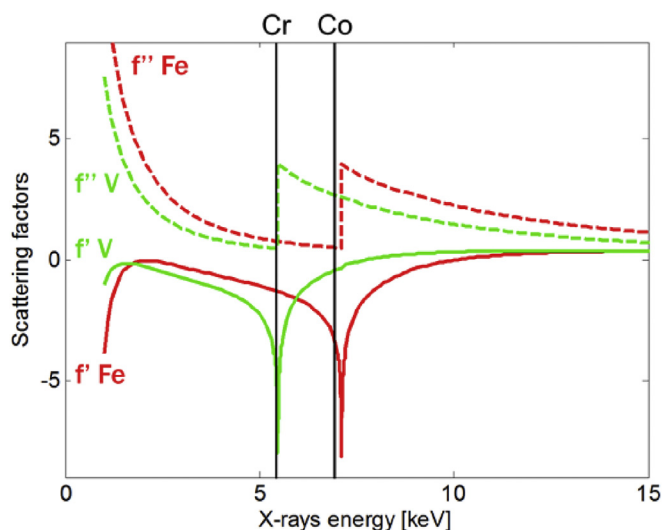

Fig. 2. Anomalous contribution to the atomic scattering factors of Fe (in red) and V (in green): f = f_0 + f' + if''. This energy-dependent contribution has a real part f' (solid lines) and an imaginary part f'' (dashed lines). The X-ray energies of Cr and Co (Kα1) sources used in this work are highlighted (Inspired by Merritt [18].). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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[1] In the $L2_1$ structure, p = 8, 6, and 12 for the (111), (200), and (220) plane families, respectively. Based on the literature, the B parameter of the temperature factor is set at 0.9 [12].