Investigation of Magnetic Ordering in RCo$_{12}$B$_6$ (R = Y, Nd) by $^{57}$Fe Mössbauer Spectroscopy*

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Abstract

Mössbauer spectra of YCo$_{12}$B$_6$ and NdCo$_{12}$B$_6$ doped with enriched $^{57}$Fe have been obtained at various temperatures between 4·2 K and room temperature. The spectrum of YCo$_{12}$B$_6$ at 4·2 K indicates that the Co sublattice orders in the crystallographic basal plane. NdCo$_{12}$B$_6$ orders along or close to the crystallographic c-axis at 4·2 K and undergoes a spin-reorientation with increasing temperature until at $\sim$55 K the magnetisation lies in or near the basal plane.

1. Introduction

The magnetic properties of the ternary rare-earth (R) intermetallics with the composition RCo$_{12}$B$_6$ have been studied by a number of groups (e.g. Jurczyk et al. 1987; Rosenberg et al. 1988; Mittag et al. 1989; Rosenberg et al. 1992; Campbell et al. 1993). These compounds crystallise in the rhombohedral SrNi$_{12}$B$_6$ structure (Niihara and Yajima 1972; Chaban and Kuz'ma 1977; Stadelmaier and Lee 1978; Kuz'ma et al. 1981) with the space group R3m. The R atoms occupy the 3a crystallographic sites, the Co atoms occupy the 18g and 18h crystallographic sites, and the B atoms occupy 18h crystallographic sites, in the standard Wyckoff notation.

Rosenberg et al. (1992) carried out a thorough investigation of the magnetic properties and $^{57}$Fe Mössbauer spectroscopy of rare-earth compounds of the type RFe$_{12-x}$Co$_x$B$_6$ ($x \leq 10$ for R = La; $x = 11·8$ for R = Y and Gd). An aim was to understand the unusual behaviour of the ferromagnetic ordering temperature exhibited by the 1-12-6 type of system compared with other systems in which cobalt is substituted for iron. For example, ferromagnetic ordering appears to vanish around $s \sim 0·25$ in the Nd(Fe$_{1-x}$Co$_x$)$_{12}$B$_6$ system, reappearing at higher cobalt concentration $s \sim 0·35$ (Buschow 1987). In the case of the LaFe$_{12-2x}$Co$_x$B$_6$ system, Rosenberg et al. (1992) linked the behaviour of the ferromagnetic ordering temperature with the unstable character of the iron moment. They further linked the partial collapse of the 3d sublattice moment at intermediate concentrations with preferential site occupation for the cobalt and iron atoms. In common with

the results obtained by Rosenberg et al. (1992) for LaFe$_{12-x}$Co$_x$B$_6$ ($x \leq 10$), YFe$_{0.2}$Co$_{11.8}$B$_6$, GdFe$_{0.2}$Co$_{11.8}$B$_6$, Campbell et al. (1993), in a $^{57}$Fe Mössbauer study of NdCo$_{12}$B$_6$ doped with enriched $^{57}$Fe, demonstrated that the Fe atoms exhibit a strong preference for occupying the 18h site rather than the 18g site. This earlier study (Campbell et al. 1993) serves as a precursor to the present study, the main purpose of which is to investigate the magnetic structures of YCo$_{12}$B$_6$ and NdCo$_{12}$B$_6$ by $^{57}$Fe Mössbauer-effect spectroscopy. The impetus for this study was the observation of an anomaly in the temperature dependence of the magnetisation of NdCo$_{12}$B$_6$ observed by Mittag et al. (1989), although quite different behaviour was observed by Jurczyk et al. (1987). Our aim was to search for a possible spin-reorientation in NdCo$_{12}$B$_6$ which may be responsible for this anomaly.

2. Experimental

The samples of YCo$_{12}$B$_6$($^{57}$Fe) and NdCo$_{12}$B$_6$($^{57}$Fe) used in this study were prepared from high-purity metals (99.9-99% Y and Nd, 99.998% Co and 99.5% B) by standard arc melting in an atmosphere of purified argon. The extent of the doping with 97.5% enriched $^{57}$Fe amounted to 0.5 wt%. The arc-melted samples were wrapped in Ta foil and annealed in sealed evacuated quartz tubes at 900°C for three weeks.

Powder X-ray diffraction (XRD) with Cu Kα radiation was used to characterise the samples. The diffraction patterns of both samples exhibited all the peaks of the rhombohedral SrNi$_{12}$B$_6$ structure (Niihara and Yajima 1972; Chaban and Kuz’ma 1977; Stadelmaier and Lee 1978; Kuz’ma et al. 1981). The lattice parameters of our samples were $a = 9.491$ Å and $c = 7.458$ Å for NdCo$_{12}$B$_6$($^{57}$Fe), and $a = 9.463$ Å and $c = 7.462$ Å for YCo$_{12}$B$_6$($^{57}$Fe). The XRD pattern of NdCo$_{12}$B$_6$($^{57}$Fe) shows the presence of Co$_2$B- and Co-type impurity phases, while the YCo$_{12}$B$_6$($^{57}$Fe) pattern shows Co$_3$B and Y$_2$O$_3$ impurities. The extent of the impurity phases will be mentioned later in the light of the Mössbauer results. Further details on the samples and their preparation are presented elsewhere (Campbell et al. 1993).

Mössbauer spectra were obtained at various temperatures between 4.2 K and room temperature (20±1°C) using a standard transmission spectrometer (Jing et al. 1992). A $^{57}$CoRh source was used in the Mössbauer experiments and the spectrometer was calibrated using an α-Fe foil at room temperature. The experimental spectra are presented relative to the centre of the α-Fe calibration spectrum.

3. Results and Discussion

YCo$_{12}$B$_6$($^{57}$Fe)

Fig. 1 shows the $^{57}$Fe Mössbauer spectra of YCo$_{12}$B$_6$($^{57}$Fe) at room temperature (Figs 1a,b) and 4.2 K (Fig. 1c). The dominant feature of the room-temperature spectrum is the central paramagnetic doublet characteristic of the 1-12-6 phase (Rosenberg et al. 1992; Campbell et al. 1993). The room-temperature spectrum on the extended velocity scale (Fig. 1a) allows us—assuming the same value of recoil-free fraction for all phases—to determine the extent of the impurity phases containing $^{57}$Fe to be ~23% of the relative area of the Mössbauer spectrum. The
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Fig. 1. $^{57}$Fe Mössbauer spectra of YCo$_{12}$B$_6$($^{57}$Fe) at (a) room temperature (extended velocity scale), (b) room temperature (low velocity scale), and (c) 4·2 K. The fits to the spectra are described in the text. The stick diagrams in (b) show the locations and relative intensities of the doublets linked with the 18g and 18h sites. Similarly, the stick diagrams labelled 18g, 18h$_1$, 18h$_2$, 18h$_3$ in the 4·2 K spectrum (c) show the location and relative intensities of the four sextets used to fit the 1-12-6 spectrum.
mean values for the hyperfine magnetic field of the impurity phase (20·3 T at room temperature and 25·0 T at 4·2 K) are consistent with the observation of the Co$_2$B($^{57}$Fe) phase in the XRD pattern (Murphy and Herschkowitz 1973).

Excluding the contribution of the Co$_2$B($^{57}$Fe) impurity phase to the experimental spectrum, the room-temperature spectrum of YCo$_{12}$B$_6$($^{57}$Fe) over the low velocity range (Fig. 1b) is well fitted by two overlapping paramagnetic doublets corresponding to $^{57}$Fe occupying the 18g and 18h crystallographic sites in the 1-12-6 structure. The locations and relative intensities of these two doublets are indicated by the stick diagrams in Fig. 1b with the relative areas, quadrupole splittings (QS) and isomer shifts (IS) of these 1-12-6 subspectra given in Table 1. The relative areas of the doublets (~89% and ~11%) have been obtained after accounting for the impurity phase, and thus refer solely to the 1-12-6 phase. As noted above, previous work on RFe$_{12-\_x}$Co$_x$B$_6$ compounds (R = La, Y, Cd) (Rosenberg et al. 1992) and NdCo$_{12}$B$_6$ (Campbell et al. 1993) showed that $^{57}$Fe exhibits a strong preference for occupying the 18h sites, and the present observed relative areas for YCo$_{12}$B$_6$ are in good accord with this result.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>QS (mm s$^{-1}$)</th>
<th>IS (mm s$^{-1}$)</th>
<th>FWHM (mm s$^{-1}$)</th>
<th>Relative area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YCo$_{12}$B$_6$</td>
<td>18g</td>
<td>0·63</td>
<td>-0·13</td>
<td>0·23</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>18h</td>
<td>0·58</td>
<td>0·10</td>
<td>0·24</td>
<td>89</td>
</tr>
<tr>
<td>NdCo$_{12}$B$_6$</td>
<td>18g</td>
<td>0·87</td>
<td>0·02</td>
<td>0·27</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>18h</td>
<td>0·64</td>
<td>0·10</td>
<td>0·27</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 2. Hyperfine interaction parameters for YCo$_{12}$B$_6$($^{57}$Fe) at 4·2 K (cf. Fig. 1c)

Errors: $B_{hf}$ ±0·5 T; QS ±0·02 mm s$^{-1}$; IS ±0·01 mm s$^{-1}$; relative area ±5%

<table>
<thead>
<tr>
<th>Component</th>
<th>$B_{hf}$ (T)</th>
<th>QS (mm s$^{-1}$)</th>
<th>IS (mm s$^{-1}$)</th>
<th>Relative area (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18h$_1$</td>
<td>14·9</td>
<td>0·04</td>
<td>0·20</td>
<td>28</td>
</tr>
<tr>
<td>18h$_2$</td>
<td>15·5</td>
<td>-0·31</td>
<td>0·20</td>
<td>22</td>
</tr>
<tr>
<td>18h$_3$</td>
<td>16·9</td>
<td>-0·45</td>
<td>0·21</td>
<td>32</td>
</tr>
<tr>
<td>18g</td>
<td>7·0</td>
<td>0·04</td>
<td>0·20</td>
<td>18</td>
</tr>
</tbody>
</table>

Fig. 1c shows the 4·2 K spectrum for YCo$_{12}$B$_6$($^{57}$Fe); at which temperature the 1-12-6 phase is ferromagnetic. Using the Mössbauer thermal scan technique we have measured the Curie temperature of YCo$_{12}$B$_6$($^{57}$Fe) and found it to be $T_C \approx 167 \pm 5$ K, in general agreement with the magnetisation measurements of Mittag et al. (1989). After subtracting the spectral contribution of the Co$_2$B($^{57}$Fe) impurity phase to the overall spectrum of Fig. 1c we find that the magnetic 1-12-6 spectrum cannot be fitted with two sextets in the relative subspectral ratio found for the two doublets in the room-temperature paramagnetic spectrum (Fig. 1b). Attempts to fit the 4·2 K spectrum with two subspectra led to unrealistically large values for the linewidths (FWHM) and even then the fit was poor. Rather, the 4·2 K spectrum of the YCo$_{12}$B$_6$ compound is well fitted with four sextets,
three of which have roughly equal areas and magnetic hyperfine fields \((B_{hf})\) differing by only about 1 T. This analysis led to physically realistic linewidth values, similar to those obtained for the analysis of the room-temperature spectra of the YCo\(_{12}\)B\(_6\) and NdCo\(_{12}\)B\(_6\) compounds (Table 1). The fourth sextet has a smaller relative area and a much smaller hyperfine field than those of the three 'primary' sextets. The relative areas and hyperfine parameters of the four 1-12-6 sextets are given in Table 2. The ratio of the combined areas of the three primary sextets to that of the fourth smaller sextet is \(\sim 82\% : 18\%\) and we can therefore assign the three primary sextets (labelled 18\(h_1\), 18\(h_2\), 18\(h_3\) in Table 2) to the 18\(h\) site, and the fourth sextet, having a much smaller hyperfine field, to the 18\(g\) site. The locations and relative areas of these four sextets are indicated by the stick diagrams in Fig. 1c. This site assignment is consistent with previous work on 1-12-6 compounds (Rosenberg et al. 1992; Campbell et al. 1993). In Campbell et al. (1993), we outlined the argument that allows us to assign the sextet having the larger hyperfine field to \(^{57}\)Fe occupying the crystallographic 18\(h\) site. Briefly, the 18\(h\) site has two more transition metal nearest neighbours than the 18\(g\) site, and one less rare-earth nearest neighbour, leading to a larger hyperfine field at the 18\(h\) site.

The observation of four sextets in the 4·2 K spectrum of the 1-12-6 phase rather than two indicates that the easy direction of magnetic ordering of the Co sublattice is not along the crystallographic \(c\)-axis and, as discussed below, is most likely to lie in the basal plane. The splitting of the 18\(h\) spectrum has been ascribed to the effects of anisotropic orbital moment contributions when the magnetisation direction is other than parallel to the \(c\)-axis (Erdmann et al. 1988). It is well known from numerous studies (e.g. Mitchell et al. 1989) that the transition metal (TM) sublattice anisotropy energy in R–TM–B ternary intermetallic phases is usually well described by a single term of the form \(K_1 \sin^2 \theta\), where \(\theta\) is the angle between the TM magnetisation and the \(c\)-axis. In the absence of other anisotropic effects this leads to magnetisation directions either parallel (\(\theta = 0^\circ\)) or perpendicular (\(\theta = 90^\circ\)) to the \(c\)-axis. Our Mössbauer results therefore suggest planar ordering of the Co sublattice in the 1-12-6 phase at 4·2 K.

\(\text{NdCo}\(_{12}\)B\(_6\)(\(^{57}\)Fe)\)

Fig. 2 shows room-temperature Mössbauer spectra of NdCo\(_{12}\)B\(_6\)(\(^{57}\)Fe) recorded over extended (Fig. 2a) and low (Fig. 2b) velocity scales. Two magnetic sextets with hyperfine fields of 31·3 T (\(\sim 18\%\) area) and 24·5 T (\(\sim 8\%\) area) are observed in these spectra and are due to \(\alpha\)-Fe-type and CoB\(_2\)(\(^{57}\)Fe)-type impurity phases. The analyses of these spectra have been presented in our previous paper (Campbell et al. 1993). Briefly, after accounting for the impurity components, the room-temperature NdCo\(_{12}\)B\(_6\)(\(^{57}\)Fe) spectrum comprises two paramagnetic doublets with relative areas \(\sim 82\%\) and \(\sim 18\%\), showing the strong 18\(h\) site preference of the \(^{57}\)Fe atoms, similar to the case of YCo\(_{12}\)B\(_6\)(\(^{57}\)Fe) described above. The location and relative intensities of these doublets are shown by the stick diagrams in Fig. 2b, with the hyperfine parameters of the NdCo\(_{12}\)B\(_6\)(\(^{57}\)Fe) spectrum at room temperature given in Table 1.

In Fig. 3 we show the Mössbauer spectra of NdCo\(_{12}\)B\(_6\)(\(^{57}\)Fe) recorded at various temperatures between 4·2 K and 175 K. As discussed previously (Campbell et al. 1993) the 4·2 K spectrum of NdCo\(_{12}\)B\(_6\)(\(^{57}\)Fe) is well fitted with two magnetic
Fig. 2. Room temperature Mössbauer spectra of NdCo$_{12}$B$_6^{(57}\text{Fe)}$: (a) extended velocity scale, and (b) low velocity scale. [See text for details of the fits; the stick diagrams in (b) show the locations and relative intensities of the 18$g$ and 18$h$ doublets.]

sextets with relative areas $\sim$81% and $\sim$19% and hyperfine fields of 15·3 T and 7·0 T, respectively. The sextet with the larger field is due to $^{57}\text{Fe}$ in the 18$h$ sites.

From inspection of Fig. 3, it is immediately apparent that, unlike the 4·2 K spectrum, the 1-12-6 component of the magnetic spectra with $T \gtrsim 55$ K cannot be fitted with two simple sextets. We have analysed these spectra in a manner similar to the analysis of the 4·2 K spectrum of YCo$_{12}$B$_6^{(57}\text{Fe)}$, i.e. in terms of three primary sextets with similar areas and hyperfine fields, corresponding to the 18$h$ site, and a fourth sextet with smaller area and field, corresponding to the 18$g$ site. Fig. 4 shows the variation of the magnetic hyperfine fields for NdCo$_{12}$B$_6^{(57}\text{Fe)}$ for the three 18$h$ sites, labelled 18$h_1$, 18$h_2$ and 18$h_3$, and the 18$g$ site as a function of temperature. The ferromagnetic ordering temperature was determined by the thermal scan technique and found to be $T_C = 168 \pm 3$ K,
Fig. 3. $^{57}\text{Fe}$ Mössbauer spectra of NdCo$_{12}$B$_6$($^{57}\text{Fe}$) at 4.2 K, 55 K, 70 K, 100 K, 135 K, 145 K and 175 K (see text for details of the fits).
agreeing well with the observed variation in $B_{hf}$ for the various sites (Fig. 4). It should be noted that the use of one sextet to represent the mean magnetic hyperfine field of the 18h site at 4·2 K, compared with the three sextets required at higher temperatures, leads to an apparent increase in the magnetic hyperfine field for the 18h$_3$ site at $T \sim 55$ K (Fig. 4).

Clearly, the magnetic ordering direction of NdCo$_{12}$B$_6$(57Fe) changes between 4·2 K and 55 K. The fact that the 4·2 K spectrum is well fitted with a single sextet due to each of the transition metal crystallographic sites indicates that the magnetic ordering direction is either parallel to the c-axis or close to it, since no magnetic splitting of the crystallographically equivalent sites is observed. Using the same argument as for YCo$_{12}$B$_6$(57Fe), the magnetic spectra of NdCo$_{12}$B$_6$(57Fe) for $T \geq 55$ K are indicative of a magnetic ordering direction in, or close to, the crystallographic basal plane.

Our Mössbauer results therefore indicate that (i) the easy magnetisation direction of the Co sublattice is in the basal plane, and (ii) NdCo$_{12}$B$_6$ undergoes a spin-reorientation from c-axis to basal plane with increasing temperature, with a spin-reorientation temperature between 4·2 K and 55 K. It should be mentioned, however, that at this stage we cannot dismiss the possibility of canted magnetic structures.

**Crystal Fields**

The axial Nd anisotropy at 4·2 K dominates the planar Co anisotropy and is related to the Nd$^{3+}$ crystal field interactions. Within the rhombohedral $R3m$
structure, the Nd occupies the 3a crystallographic site with point symmetry 3m. Thus the Nd$^{3+}$ crystal field Hamiltonian may be written (in standard notation) as

$$\mathcal{H} = B_{20}O_{20} + B_{40}O_{40} + B_{43}O_{43} + B_{60}O_{60} + B_{63}O_{63} + B_{66}O_{66}. \quad (1)$$

We note here that rhombohedral structures are often indexed in terms of a hexagonal lattice. Nevertheless, the ‘hexagonal’ crystal field Hamiltonian, in which $B_{66}O_{66}$ is the only off-diagonal term, is inappropriate for rhombohedral structures.

The only crystal field information available on the RCo$_{12}$B$_6$ compounds at present is due to Gubbens et al. (1990) who fitted the temperature dependence of the $^{166}$Er hyperfine magnetic field and quadrupole splitting deduced from $^{166}$Er Mössbauer measurements on ErCo$_{12}$B$_6$. Using a simple exchange plus diagonal crystal field Hamiltonian, Gubbens and coworkers deduced the following crystal field parameters (relevant to Er$^{3+}$):

$$B_{20} = -0.39 \text{ K}; \quad B_{40} = -0.5 \times 10^{-2} \text{ K and } B_{60} = -0.2 \times 10^{-4} \text{ K.}$$

These parameters can be scaled to give the corresponding Nd$^{3+}$ parameters if one assumes no change in the relevant crystal field lattice summations, such as $A_{20}$ (standard notation). Using the appropriate Stevens (1952) constants and the 4f electronic radial averages (Freeman and Desclaux 1979), we deduce the following Nd$^{3+}$ parameters:

$$B_{20} = +1.54 \text{ K}; \quad B_{40} = +7.5 \times 10^{-2} \text{ K and } B_{60} = +1.02 \times 10^{-4} \text{ K.}$$

However, these parameters predict a basal plane ordering of NdCo$_{12}$B$_6$ at 4.2 K and so are inconsistent with our experimental observations.

We have carried out point-charge model calculations for the R$^{3+}$ ions in the RCo$_{12}$B$_6$ structure, and these predict that $A_{20} < 0$. Hence, $B_{20}$ should be positive for Nd$^{3+}$, in agreement with the above deduction based on the ErCo$_{12}$B$_6$ work of Gubbens et al. (1990). In order to get axial ordering of NdCo$_{12}$B$_6$ at low temperatures, we therefore need $B_{40}$ and/or $B_{60}$ to be negative, opposite to the deduced values above. We note that the temperature dependence of the $^{166}$Er hyperfine data reported by Gubbens et al. (1990) are low-temperature values up to $T/T_c \sim 0.35$, and that the off-diagonal crystal field terms in equation (1) were ignored. Furthermore, the $^{166}$Er spectra are complicated by electronic relaxation effects.

Clearly, more experimental data on the RCo$_{12}$B$_6$ compounds are required to enable us to determine a set of crystal field parameters appropriate to this phase. For example, we have shown that the Co sublattice exhibits easy-plane anisotropy, whereas Gubbens et al. (1990) claim c-axis ordering in ErCo$_{12}$B$_6$ at low temperature. Hence, as rare-earth anisotropy generally decreases faster than transition metal anisotropy with increasing temperature, it is likely that ErCo$_{12}$B$_6$ will exhibit a spin-reorientation. Data such as spin-reorientation temperatures provide invaluable information for the determination of crystal field parameters.
4. Conclusions

On the basis of $^{57}$Fe Mössbauer-effect spectroscopy of NdCo$_{12}$B$_6$ and YCo$_{12}$B$_6$ doped with enriched $^{57}$Fe, we have shown that the Co sublattice anisotropy in the RCo$_{12}$B$_6$ compounds is planar. At 4·2 K, NdCo$_{12}$B$_6$ orders along or close to the crystal c-axis, and undergoes an axis–plane spin-reorientation in the temperature range 4·2–55 K. At this stage the possibility of canted magnetic structures cannot be ruled out.

Acknowledgments

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References


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A Heuristic Account of the Electron–Phonon Coupling Mechanism in the Formation of Pre-martensite Tweed Structures*

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Abstract
Electron–phonon coupling has been proposed by a number of researchers as the probable mechanism involved in martensitic transformations of many metals and alloys. This paper provides a plausible account of the way in which Kohn anomalies may give rise to tweed microstructure in pre-martensitic phases of fcc and bcc crystals.

1. Introduction

The purpose of this paper is to demonstrate the way in which the periodic lattice displacements of tweed structure may be formed as the result of Kohn anomalies in both bcc and fcc crystals. Essentially, this demonstration is presented in diagrammatic form so that the relationships between the representations in direct and reciprocal space may be clearly seen. This work is an extension of the ideas of Krivoglaz (1969), Krivoglaz and Tu Hao (1968) and Moss (1969) who considered pre-martensitic anomalies in various alloys.

In the electron–phonon interaction mechanism outlined by Ashcroft and Mermin (1976) and Ziman (1969), the basic assumption is that the rate of sound attenuation associated with the lattice softening is related to the energy being lost by the phonons to the Fermi-surface electrons. This is so because when a sound wave propagates through a metal the microscopic electric fields due to the displacement of the ions can impart energy to electrons near the Fermi level, thereby removing energy from the wave. It should be noted that it is only those electrons near the Fermi surface that can affect the sound attenuation, since the exclusion principle forbids electrons with lower energies from exchanging small amounts of energy with the waves. Furthermore, it is the electrons near the external Fermi surface that play a dominant role since there are many more of them.

Axe and Shirane (1973) illustrated their discussion of displacive transformations in terms of the soft-mode concept with a simple one-dimensional representation of a longitudinal displacement wave in a periodic lattice with spacing $a$. They considered the case when the magnitude of the phonon wavevector $q$ is equal to $\pi/a$ so that the displacements of adjacent atoms are out of phase, as shown in Fig. 1. Such fluctuations with harmonic time dependence are Brillouin

zone-boundary phonons, and static displacements or displacive transformations can result if they become unstable. Axe and Shirane (1973) showed that, for the particular zone-boundary phonon pictured in Fig. 1, the associated displacive transformation involves a ‘dimerisation’ of the lattice particles and a doubling of the unit cell dimension, as shown in Fig. 2. This particular case has been thoroughly investigated by Peierls (1955) and the role of the Fermi surface has particular significance.

![Fig. 1. Zone-boundary longitudinal phonon with wavevector \( q = \pi/a \) in a periodic one-dimensional lattice.](image1)

![Fig. 2. ‘Dimerisation’ of lattice particles in a periodic one-dimensional lattice resulting from the displacive transformation produced by the softening of the zone-boundary phonon shown in Fig. 1.](image2)

In Sections 2 and 3 the basic principles of this illustration are used to explain the displacive transformations associated with a bcc alloy and a fcc alloy in terms of (110) and (111) transverse acoustic phonons respectively. Whereas Axe and Shirane (1973) accounted for the displacive transformation of ‘dimerisation’ in terms of the static displacement of single atoms in opposite directions, it is intended in the next sections to provide similar explanations of the formation of tweed microstructures in terms of the static displacement of large groups of atoms in the same direction.

In discussing structural phase transformations, the range of correlations between the atomic displacements induced by a soft mode is designated as the correlation length \( \zeta \). Furthermore, the size of \( \zeta \) is indicated in the corresponding diffraction patterns by the thickness \( 2\pi/\zeta \) of the relwalls of diffuse scattering. It has already been shown by Norman et al. (1985) and Finlayson et al. (1988) that the thickness of the diffraction relrods of Cu51Zn49 and Fe98Ni32 may be modelled by Kohn constructions. In the following sections it will be shown that the correlation lengths of the displaced atoms of each of these alloys are thereby related to the degree of overlap of the corresponding multiply-connected Fermi surfaces.

2. Electron–Phonon Coupling in the bcc Alloy Cu51Zn49

Fig. 3 is the reciprocal lattice diagram of Cu51Zn49 and includes the Fermi surface and related Brillouin zone boundaries depicted in the (010) plane. Also
shown is the solid arrow representing the $\langle 101 \rangle \langle 10\bar{1} \rangle$ transverse acoustic (TA) phonon satisfying the Kohn anomaly condition $q = 2k_F$, and the broken arrow representing the Fermi surface electron wavevector $k_F$ in the $\langle 101 \rangle$ direction.

![Reciprocal lattice diagram](image)

Fig. 3. Reciprocal lattice diagram of $\beta$-Cu$_{51}$Zn$_{49}$ in the $\langle 010 \rangle$ plane showing the Fermi surface and Brillouin zone boundaries. The Kohn anomaly wavevector $q = 2k_F$ is represented by the solid arrow.

Fig. 4 is the crystal lattice diagram of Cu$_{51}$Zn$_{49}$ showing the same two vectors as in Fig. 3. It can readily be seen that the phonon involves simultaneous displacements of atoms in $\langle 101 \rangle$ rows in $\langle 10\bar{1} \rangle$ directions. It is suggested that it is in this way that the large number of atoms constituting each of the basic units of a tweed pattern are displaced when pre-martensitic conditions prevail in this alloy. In this regard it is of particular interest to note that Figs 3 and 4 clearly indicate how the value of $\lambda$ results in this phonon gradually getting out of phase with the periodicity of the crystal lattice in $\langle 101 \rangle$ directions. This is so because in Fig. 3 $q = 2k_F,\langle 101 \rangle$ is slightly larger than the spacing between 000 and 101 because $k_F,\langle 101 \rangle$ extends slightly beyond the Brillouin zone boundary. Accordingly, in Fig. 4 $\lambda$ is slightly less than the interatomic spacing in the $\langle 101 \rangle$ direction.

It is therefore suggested that if the Fermi surface extends beyond the Brillouin zone boundary in the $\langle 101 \rangle$ direction by 1/50 of the distance from 000 to this boundary, then the pair of anti-phase domain boundaries corresponding to the opposite edges of a tweed cell would be 50 atoms apart.

Such pre-martensitic structural modulations may constitute nucleation sites for martensitic transformations. When $\beta$-brass is quenched, it rapidly orders to form the $\beta^1$ phase and simultaneously undergoes a martensitic transformation by forming plates of a close-packed structure which is basically fcc. The nucleation
and growth of a martensite plate is a complex process which takes place in several distinct stages. Of particular significance for this nucleation is (101) \langle 10 \bar{1} \rangle shear. The stiffness of a bcc structure, such as \( \beta \)-brass, with respect to (101) \langle 10 \bar{1} \rangle shear is given by the elastic modulus \( c' = 0.5(c_{11} - c_{12}) \), and the ratio of \( c' \) to \( c_{44} \) is a measure of stability with respect to a close-packed structure. For

Fig. 4. Crystal lattice diagram of \( \beta \)-Cu_{51}Zn_{49} in the (0\bar{1}0) plane showing the Kohn anomaly phonon with wavelength \( \lambda \).

\[
\begin{align*}
\bar{2}22 & \quad \circ \quad 002 & \quad \circ \quad 222 \\
\bar{1}11 & \quad \circ \\
\bar{2}20 & \quad \circ \\
\bar{1}11 & \quad \circ \\
\bar{2}22 & \quad \circ \\
00\bar{2} & \quad \circ \\
222 & \quad \circ
\end{align*}
\]

Fig. 5. Reciprocal lattice diagram of Fe_{98}Ni_{32} in the (1\bar{1}0) plane showing the Fermi surface and Brillouin zone boundaries. The Kohn anomaly wavevector \( q = 2k_F \) is represented by the solid arrow.
β-brass, $c'/c_{44} = 1/18$ at room temperature. The absolute value of $c'$ is low and it decreases as the temperature falls towards the transformation temperature, indicating that the resistance of the lattice to (101) (101) shear is small at the temperature of its transformation to a close-packed structure.

3. Electron–Phonon Coupling in the fcc Alloy Fe$_{68}$Ni$_{32}$

Fig. 5 is the reciprocal lattice diagram of Fe$_{68}$Ni$_{32}$ and includes the Fermi surface and related Brillouin zone boundaries depicted in the (110) plane. A significant (111) (112) TA phonon is also shown in a manner similar to the representation of (101) (101) phonons in Fig. 3.

Fig. 6 is the (110) crystal lattice diagram of Fe$_{68}$Ni$_{32}$. As in the case of Cu$_{51}$Zn$_{49}$ it can be seen how the boundaries of a tweed cell in Fe$_{68}$Ni$_{32}$ may arise as a (111) (112) TA phonon that satisfies the Kohn anomaly condition extends to atoms where the (112) displacements are out of phase with those shown in Fig. 6.

Because (112) displacements on {111} planes in fcc structures are geometrically equivalent to (101) displacements on {101} planes in bcc structures, it is suggested that pre-martensitic nuclei in Fe–Ni alloys may be generated by the static atomic displacements produced by electron–phonon coupling in the same way as may occur in Cu–Zn alloys.

![Fig. 6. Crystal lattice diagram of Fe$_{68}$Ni$_{32}$ in the (110) plane showing the Kohn anomaly phonon with wavelength $\lambda$.](image)

4. Conclusion

The brief analysis outlined above appears to indicate the way in which electron–phonon coupling may give rise to the formation of tweed structure in both Cu$_{51}$Zn$_{49}$ and Fe$_{68}$Ni$_{32}$ alloys. It seems reasonable to suggest that the same mechanism may also be applicable to all those crystals that possess multiply-connected Fermi surfaces and exhibit tweed structure.
References


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