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LETTER TO THE EDITOR

Ni diffusion in the high-temperature intermetallics Ni₃Sb studied by quasielastic neutron scattering

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Abstract. Nickel diffusion in the high-temperature phase of the intermetallic alloy Ni₃Sb is extremely fast compared to diffusion in other intermetallics. We have studied quasielastic neutron scattering, which permits us to determine the elementary diffusion mechanism on an atomic scale. A model explaining diffusion by Ni jumps between the α - and γ -Ni sublattices of the DO_3 (Fe₃Si) structure has been tested and satisfactory agreement has been obtained.

Diffusion in intermetallic alloys is interesting not only because jumps on an ordered structure represent an attractive physical problem, but also because diffusion is relevant for the high-temperature properties of these alloys. Recently the elementary diffusion mechanisms in three intermetallics have been determined by use of atomistic techniques: in the cubic alloys FeAl (Sepiol and Vogl 1993a) and Fe₃Si (Sepiol and Vogl 1993b) by quasielastic Mössbauer spectroscopy and in hexagonal NiSb (Vogl *et al* 1993) by quasielastic neutron scattering. It is particularly interesting that at comparable temperatures on a reduced scale the diffusion of the majority component in intermetallics with DO_3 (Fe₃Si) structure is much faster than diffusion in other intermetallics and also considerably faster than diffusion of the minority component (Wever *et al* 1989). We have chosen Ni₃Sb for the present study because even among all the DO_3 alloys hitherto studied Ni diffuses fastest, as was found several years ago by Heumann and Stüer (1966) in measurements of the tracer diffusion. The diffusivity of Sb has not yet been determined.

The DO_3 phase of Ni₃Sb (figure 1) is a high-temperature phase, stable above about 530 °C (Heinrich *et al* 1978). An interesting feature of the phase diagram is the fact that the melting point in the relevant region has a maximum at about 27.5 at.%Sb. Some authors therefore write Ni₅Sb₂ instead of Ni₃Sb (Massalski 1986). There is considerable confusion in the literature concerning the structure of the Ni₃Sb high-temperature phase, Ishida *et al* (1985) claiming a phase diagram that in the region of 25 at.%Sb deviates strongly from Heinrich's data. We have therefore performed high-temperature diffraction studies with x-rays and neutrons and have confirmed that Ni₃Sb had DO_3 structure at temperatures above about 530 °C. The neutron scattering study indicated that the excess of Sb atoms in Ni_{72.5}Sb_{27.5} is compensated by vacancies on the α sublattices with a ratio of occupancy of the γ and of each of the α sublattices of $c_\gamma/c_\alpha = 1.25$. This may be compared with the results of Heumann and Stüer (1966) who deduced that at 750 °C the total Ni vacancy concentration was of the order of 10%. Detailed results on the structure will be reported in a separate paper (Randl *et al* 1994a, b).

Single crystals of Ni_{72.5}Sb_{27.5} were grown by the zone-melting technique from high-purity alloy material (Ni 5N, Sb 4N5) in a combined growth-and-measuring furnace

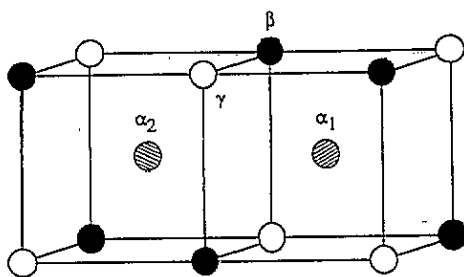


Figure 1. The $D0_3$ structure of Ni_3Sb ($2/8$ of the elementary cell). The Ni atoms occupy the sublattices α_1 , α_2 and γ , the Sb atoms the sublattice β . In case of Sb excess, vacancies are created on the α sublattices.

(Flottmann *et al* 1987, Vogl *et al* 1989). Since the crystals were destroyed by cooling below 530°C we grew one crystal directly on the three-axes spectrometer IN3 of the Institut Laue-Langevin in order to control the crystal quality and to determine the orientation. The furnace was subsequently transferred to the backscattering spectrometer IN10 without intermediate cooling of the crystal. The diffusion measurements were performed for three different crystal orientations relative to the incoming neutron beam, with one orientation at two different temperatures (700°C and 800°C). The measuring procedure and the definition of the Euler angles for describing the orientation were the same as defined in an earlier paper in this journal (Vogl *et al* 1993).

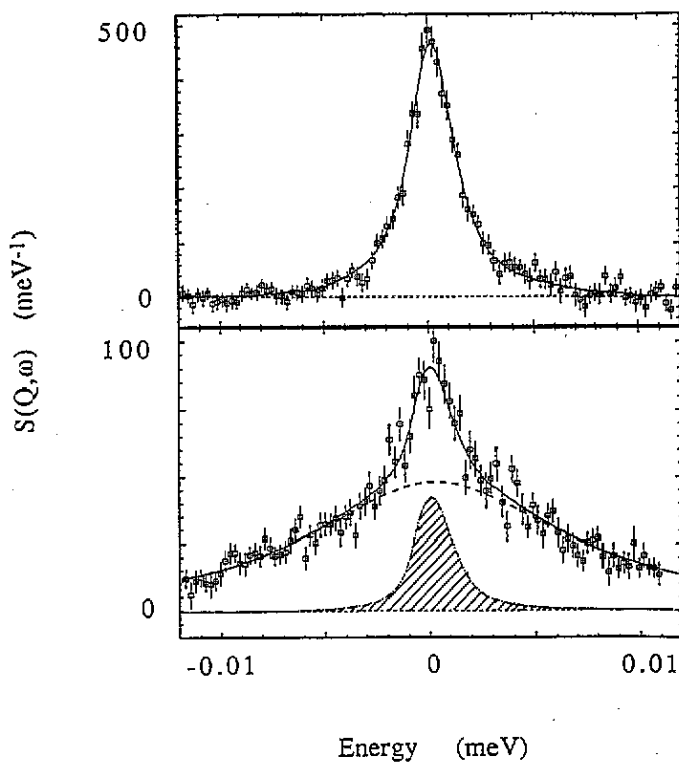


Figure 2. Quasielastic neutron scattering spectra for a $\text{Ni}_{72.5}\text{Sb}_{27.5}$ crystal oriented relative to the neutron beam as described by the Euler angles $\Phi = 120^\circ$, $\Theta = 5^\circ$, $\Psi = 135^\circ$ (Euler angles as defined by Vogl *et al* 1993); the upper and lower panels correspond to $Q = 0.41 \text{ \AA}^{-1}$ and $Q = 1.82 \text{ \AA}^{-1}$. $T = 800^\circ\text{C}$.

Figure 2 shows spectra for two different values of the momentum transfer Q . Whereas for small absolute values of Q , i.e. in the hydrodynamic regime, fits with one broadened line are sufficient, this is no longer true for $|Q| = Q > 1 \text{ \AA}^{-1}$. There the atomistic details of the jumps become important.

How to calculate the quasielastic line widths due to jumps between sublattices of ordered structures has been summarized in a recent paper (Randl *et al* 1994a, b). The particular case of jumps on a DO_3 lattice has also been investigated quite recently: in a study of Fe diffusion in DO_3 -ordered Fe_3Si Sepiol and Vogl (1993b) have found that the Fe atoms jump exclusively via vacancies on the α and γ sublattices, avoiding the β sublattice which is 'reserved' for the Si atoms. In the following we shall investigate whether that model also holds for $Ni_{72.5}Sb_{27.5}$.

Following Sepiol and Vogl (1993a, b) for the particular case of the DO_3 structure and jumps between the Ni sublattices a 3×3 jump matrix has to be diagonalized that takes into account the different jump possibilities between the three different Ni sites in the DO_3 unit cell. In the calculations our knowledge on the occupation of the different sublattices of $Ni_{72.5}Sb_{27.5}$ was taken into account, in particular that a higher fraction of the α sites than of the γ sites is vacant. (From detailed balance it follows that $c_\gamma/c_\alpha = \tau_\gamma/\tau_\alpha$ where τ_γ is the residence time on a site of the γ sublattice before jumping to the α sublattice and τ_α is the residence time on a site of each of the α sublattices before jumping to the γ sublattice.)

The resulting eigenvalues and eigenvectors of the jump matrix give the quasielastic widths and the weights of the three diffusionally broadened Lorentzians that superpose in the quasielastic signal. Both the quasielastic line widths and the weights depend on the momentum transfer Q to the neutron. It turned out that in all cases examined, a fit with two instead of three lines, i.e. with a narrow line and a broad line, was sufficient since at each value of Q one of the lines has practically no intensity.

We compared experiment and theory in the following way. The widths of the two lines with significant weights were calculated. Two Lorentzians were then fitted to the data for $Q > 1 \text{ \AA}^{-1}$ keeping the relative weights fixed to each other in the ratio required by the model. The Q -dependences of the line with the smaller width were compared with the theoretical values. Figure 3 give such a comparison for all three orientations of the single crystal. There is no obvious discrepancy between theory and experiment, i.e. *a model for jumps exclusively between α and γ sites describes the data*. However, statistical errors are large; therefore a distinction between jump models differing only in detail appears currently impossible, in particular since the width of the broad line could be determined only with low accuracy due to the problem of background separation.

The line width at small Q (hydrodynamic lines) is connected to the diffusivity D through

$$\lim_{Q \rightarrow 0} \Gamma = 2\hbar D Q^2.$$

The macroscopic diffusivity can therefore be derived from the Q -dependence of the line width at small Q . We obtain

$$D(700 \text{ }^\circ\text{C}) = 3(1) \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \quad D(800 \text{ }^\circ\text{C}) = 6(2) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}.$$

These values agree reasonably well with the diffusivities determined from tracer diffusion measurements by Heumann and Stürer (1966):

$$D(700 \text{ }^\circ\text{C}) = 2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \quad D(800 \text{ }^\circ\text{C}) = 5 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}.$$

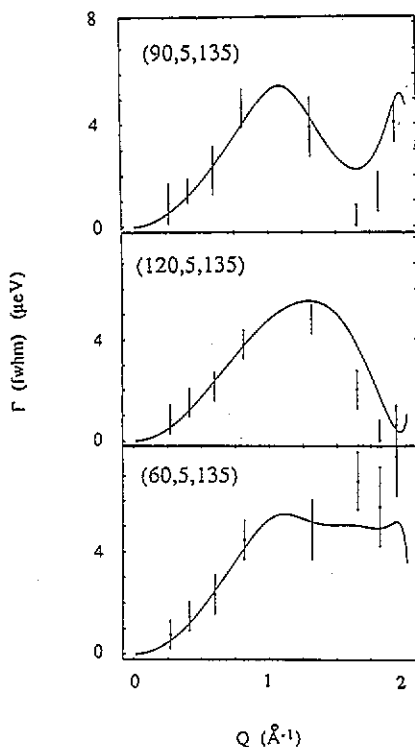


Figure 3. The dependence of the width of the narrower quasielastic line on Q for three crystal orientations. Euler angles (Φ , Θ , Ψ) as defined by Vogl *et al* (1993). Lines: the theoretical expectation for the model described in the text; dots with error bars: the experimental data points. $T = 800$ °C.

Comparing the results for Fe_3Si (Sepiol and Vogl 1993b) and $\text{Ni}_{72.5}\text{Sb}_{27.5}$, both with $D0_3$ structure, we conclude that *jumps between α and γ sublattices are the principal mechanism for the surprisingly fast diffusion of Fe and Ni atoms in the $D0_3$ structure*. In $\text{Ni}_{72.5}\text{Sb}_{27.5}$, Ni diffusion is particularly fast—about a hundred times faster still than Fe diffusion in Fe_3Si . This certainly has to do with a very high vacancy concentration on the Ni sublattices.

We thank H Wever for drawing our attention to the NiSb system, W Miekeley for preparing parts of the master alloys, M Mantler for support with the determination of the structure by way of high-temperature x-ray diffraction and H Schober for enabling the use of IN3 for crystal orientation.

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