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The order–disorder transition in supersaturated $Zr_{100-x}Al_x$ studied by inelastic neutron scattering

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Abstract

We have studied the influence of supersaturating Zr by Al on the atomic dynamics of the supersaturated solid solution using inelastic neutron scattering before and after the order–disorder transition. The samples ($x = 5$, 10 and 20 at.%) were characterized by X-ray diffraction and differential scanning calorimetry (DSC). From the neutron scattering data the generalized vibrational density of states (GVDOS), and the dynamic structure factors were determined in all cases. We find a small but distinct weakening of the lower energy (transverse) modes on supersaturation. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Order to disorder transitions (ODT) can be observed using different production techniques [1–3], which constrain the system to form metastable phases. The ODT was also successfully simulated by MD calculations [4,5]. Mechanical alloying of Zr and Al can results in an hcp supersaturated solid solution, and in an amorphous solid, depending on the concentration [6,7]. Therefore the ZrAl system is especially favourable for studying this order–disorder transition. The ODT is accompanied and most likely caused by a reduced resistivity against shear fluctuations in the sample [4,5]. We therefore expect, with a stronger supersaturation, to observe a softening of transverse modes, and an enhanced vibrational part of the specific heat at low temperatures.

2. Experimental details

The samples with nominal Al concentration of 5, 10 and 20 at.% were prepared by mechanical alloying in a planetary ball mill (Pulverisette 5), using stainless steel vial and balls. To avoid the contamination by hydrogen and other impurities, elemental powders of pure Zr (100 mesh, 99.8%) and Al (60 μm, 99.9%) were mixed with a chosen nominal composition and sealed in the milling vial under argon atmosphere in a high purity glove box.

2.1. X-ray diffraction, differential scanning calorimetry (DSC)

From the X-ray diffraction pattern (Fig. 1), we determined that the two samples with lower

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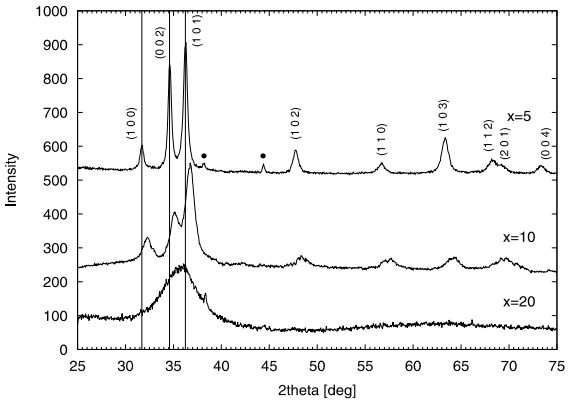

Fig. 1. X-ray diffraction pattern of $Zr_{100-x}Al_x$. The vertical lines makes clear the peak shiftening, the points indicate the peaks of the Al sampleholder.

Al concentration ($x = 5$, 10) are still crystalline, with crystal sizes of 15–20 and 5–10 nm, respectively. A decrease of the hcp lattice parameters (peak shiftening, expressed by the vertical guide lines in Fig. 1) clearly reflects the enhanced amount of Al in the Zr crystals, when the nominal and average Al concentration of the sample is higher. The third sample ($Zr_{80}Al_{20}$) forms an amorphous solid, confirmed by the structureless diffraction halo. The small peaks (indicated with filled circles on Fig. 1) are due to the Al sample holder, as we know from repeated scans at this angle. No observable amount of impurity is present.

In the case of $Zr_{95}Al_5$ the DSC scan shows no supersaturation (demixing on heating), which indicates thermodynamic stability of the material, e.g. the Zr lattice is not yet supersaturated with Al, although it is already expected at this composition. Probably the Al concentration in the crystals is lower than the average composition, and correspondingly higher at the grain boundaries. The DSC curve of $Zr_{80}Al_{20}$ shows a sharp demixing peak at 769 K, and one at 839 K, which corresponds to crystallization (concluded from X-ray diffraction measurements, after having heated up the samples between and beyond the DSC peaks). In case of $Zr_{90}Al_{10}$ only one broadened peak at 787 K is observed, which includes both demixing and crystal growth.

2.2. Neutron scattering

The inelastic neutron scattering measurements were performed at the spallation neutron source ISIS at the thermal neutron time-of-flight spectrometer MARI, at 200 K. An incident energy of 55 meV and scattering angles between 3.4 and 134.1° were used, leading to the maximum momentum transfer of 95 nm^{-1}. The energy resolution, as obtained from the FWHM of the elastic peak in the vanadium calibration spectra, was 2.4 meV.

Having applied all necessary corrections (except that for the finite resolution of the spectrometer and multiple scattering of neutrons in the sample) the generalized vibrational density of states (GVDOS) [8] was determined from the measured spectra. From the corresponding Debye frequency, the Debye temperature (Θ_D) can be calculated [8]. Likewise the vibrational part of the specific heat in the harmonic approximation can be calculated using $G(\omega)$ in place of the phonon density of states $f(\omega)$ (Eq. (1)).

$$C_v(T) = 3R \int_{\beta_{min}}^{\beta_{max}} \frac{\beta^2 e^{\beta}}{(e^{\beta}-1)^2} G(\beta)\,d\beta, \quad \beta = \frac{\hbar\omega}{k_B T}. \tag{1}$$

β_{min} and β_{max} are calculated from the frequency limits of the GVDOS [8]. At low temperatures C_v follows a T^3 law. The fitted coefficient is proportional to Θ_D^{-3}.

3. Results

All GVDOS (Fig. 2.) consist of two main bands centered at about 17 and 33 meV. The low energy part of the GVDOS (below 4 meV, shown on Fig. 2 as a vertical line) is covered by the foot of the elastic peak. Thus the data in this energy region were replaced by the Debye spectra, fitted to the measured data. The calculated specific heat increases with T^3 up to about 18, 22, 15 K in case of $x = 20$, 10, 5, respectively. Below approximately 27 K the samples with higher Al concentration have an increased vibrational contribution to the specific heat, and correspondingly a lower Debye temperature.

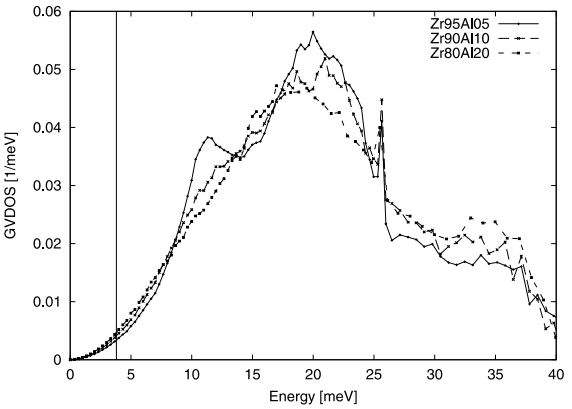

Fig. 2. GVDOS of $Zr_{100-x}Al_x$ for $x = 5$, 10 and 20. The vertical line shows the energy region where the inelastic spectrum could not be separated from the foot of the huge elastic peak. The extremly sharp peak at about 25.5 meV (one time channel only!) is an artefact.

4. Discussion

Based on the concentrations and on the atomic masses we assume, that mostly Al atom vibrations contribute to the band at higher energies, and the one at lower energies is dominated by Zr atom vibrations. The band at lower energies shows significant differences. It is split into two parts in case of $Zr_{95}Al_5$, and transforms into one peak with a shoulder on supersaturating the Zr lattice with Al atoms. We assume that this broadening effect is due to the different milling parameters (which can influence the quantity and quality of the grain boundaries, stresses and dislocations). Since the presence of the Al atoms in the Zr lattice is kind of a structural defect, we assume that the supersaturation further broadens the frequency distribution. As expected, in the low energy region, the amorphous sample has the highest, and the sample with lowest Al concentration has the lowest intensity (up to 8–9 meV).

5. Conclusion

The chosen compositions have a variation of Al content from 5 to 20 at.%. The samples with stronger supersaturation (and smaller crystal size) have enhanced intensity of GVDOS at low energies, inspite of increasing the proportion of light atoms with increasing supersaturation. We observe a corresponding increase of the vibrational part of the specific heat at low temperatures and a lowering of the Debye temperature. We have also determined the dynamic structure factor of the three samples and, with this, the wavelength dependence of the atomic dynamics. It shows considerable softening of the vibrational spectra, as the Al concentration increases. We interpret this observation as a predominant softening of the transverse modes, i.e. a weakening of the restoring forces on an atomic level and on phonon wavelength scale on supersaturation of Zr with Al.

Acknowledgements

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