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Vibrational properties of $MgZn_2$

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Abstract. We present here simulation results on the dynamical structure factor of the C14 Laves Phase of $MgZn_2$, the simplest of the Mg–(Al,Zn) Frank-Kasper alloy phases. The dynamical structure factor was determined in two ways. Firstly, the dynamical matrix was obtained in harmonic approximation from ab-initio forces. The dynamical structure factor can then be computed from the eigenvalues of the dynamical matrix. Alternatively, Molecular Dynamics simulations of a larger sample were used to measure the correlation function corresponding to the dynamical structure factor. Both results are compared to data from neutron scattering experiments. This comparison also includes the intensity distribution, which is a very sensitive test. We find that the dynamical structure factor determined with either method agrees reasonably well with the experiment. In particular, the intensity transfer from acoustic to optic phonon modes can be reproduced correctly. This shows that simulation studies can complement phonon dispersion measurements.

1. Introduction

Magnesium and zinc form alloys in different degrees of complexity up to the decagonal and icosahedral quasicrystals in the Mg–(Al,Zn) Frank-Kasper alloy system. This system is therefore ideal to study the influence of increasing complexity on the vibrational properties of an alloy. As a first step in such a study, we start here with the relatively simple Laves phase $MgZn_2$.

The lattice dynamics of the $MgZn_2$ phase has been previously studied by inelastic neutron scattering on a single grain crystal (see [1] for experimental conditions). Both the dispersion relation and the normalized intensity [1] have been reported. Two very different behaviors have been observed for the transverse acoustic (TA) mode. For TA modes propagating along the TT′ direction, polarised along the *c* axis, there is a strong bending of the dispersion curve with a maximum energy of 1.7 THz. At the same time there is a strong coupling of the TA mode with a higher energy optical mode, with an intensity transfer from the TA to the optic mode. For TA modes propagating along the Δ direction, polarised in the hexagonal plane, the dispersion relation reaches a much higher energy equal to 2.6 THz, and the normalized intensity remains almost constant.

We compare these experimental observations with two different methods to compute both the dispersion relation and the intensity distribution, which is a much tougher test than the dispersion relation alone. In the first method, the dynamical structure factor can be obtained from the eigenvalues of the dynamical matrix determined in harmonic approximation (Section 2). In principle, this method can be used also with classical interaction potentials, but in our case we determine the dynamical matrix from ab-initio forces, which should result in the best possible accuracy.

In a second method, the dynamical structure factor is interpreted as a certain correlation function, which can be measured in a molecular dynamics (MD) simulation (Section 3). This requires much larger samples, prohibiting the direct use of ab-initio methods. Classical interaction potentials are therefore necessary. For the best possible reliability, these potentials are fitted to reproduce ab-initio data, however. The possibility of using larger samples has also the advantage, that structural or occupational disorder can be taken into account, which may prove useful for the more complex structures in the Zn–Mg system.

2. Ab-initio calculations

The Laves phase of $MgZn_2$ has 12 atoms in the primitive unit cell, so that ab-initio calculations can be performed relatively easily, using the VASP code [2, 3] with the PAW method [4]. The relaxed unit cell is promoted to an

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orthorhombic supercell with 48 atoms and relaxed again. The dynamical matrix in harmonic approximation is then determined by displacing one atom at a time (by ± 0.05 Å), and computing the resulting forces on all other atoms. This has to be repeated for 12 independent displacements and is most conveniently done by using the PHONON package [5], which generates the configurations for VASP with the required displacements, and computes and diagonalizes the dynamical matrix from the VASP forces. The coherent part of the dynamical structure factor is then given by

$$S_c(q,\omega) \propto \sum_s F_s(Q,q)\,\frac{1}{\omega}\,(n(\omega,T)+1) \times \delta(Q-Q_B-q)\,\delta(\omega-\omega_s(q))\,, \qquad (1)$$

where $Q = k_f - k_i$ is the total momentum transfer, Q_B the Bragg peak corresponding to elastic scattering, q the phonon wave vector, and $\hbar\omega_s = E_f - E_i$ the energy transfer. $n(\omega,T)+1$ is a thermal occupation factor, and $F_s(\vec{Q},\vec{q})$ is the coherent form factor, which is also determined within PHONON. The sum runs over all $3N$ vibrational modes.

In order to account for the instrumental resolution, $S_c(q,\omega)$ has been convoluted with a Gaussian, whose width was chosen so as to obtain the best fit with experiment. The final comparison is shown for the two directions $\xi,\xi,6$ and $2,2,\xi$ in reciprocal space (Fig. 1 and Fig. 2). This means that the scans in Q-space are started at the Bragg peaks $Q_B = 0,0,6$ and $Q_B = 2,2,0$, and proceed along the directions $q = \xi,\xi,0$ and $q = 0,0,\xi$, respectively. The graphs show the results for selected values of ξ; the corresponding magnitudes of q are indicated in the upper right corner of each subgraph. To obtain this comparison, a constant background was added to the calculated intensities, which were also uniformly rescaled for

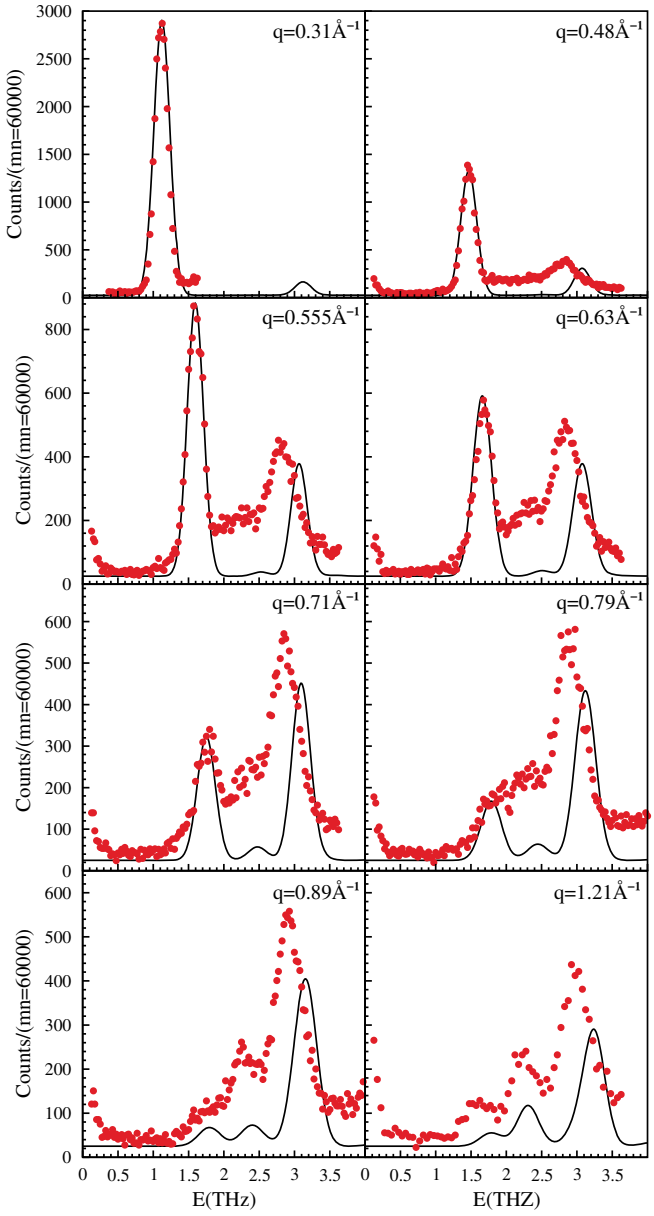

Fig. 1. Measured (circles) and calculated (solid line) intensities for direction $\xi,\xi,6$ (TT′) for eight different q values. The errorbars in the measurement are smaller than the symbol size.

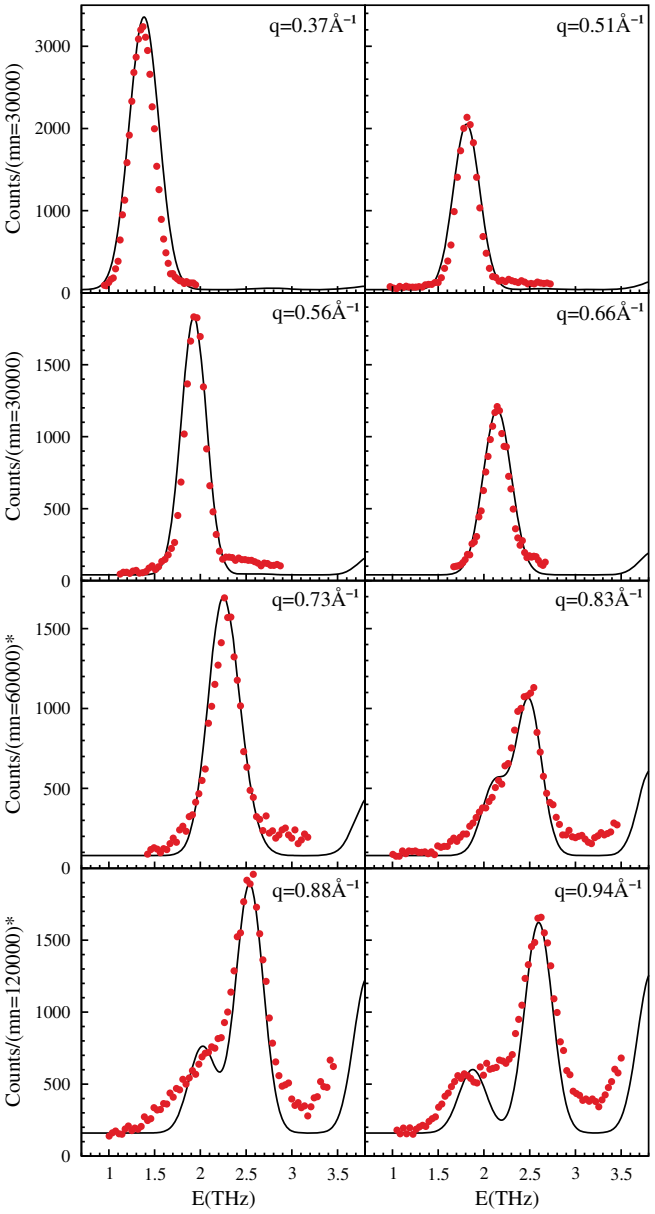

Fig. 2. Measured (circles) and calculated (solid line) intensities for direction $2,2,\xi$ (Δ) for eight different q values. The errorbars in the measurement are smaller than the symbol size. An asterisk at the y-label of a graph means that the left graph was rescaled to the indicated monitor.

each direction. Furthermore, for both directions the energies (frequencies) had to be rescaled by a constant factor of 1.14 and 1.08, respectively. This seems to indicate that the sound velocities are not accurately reproduced by the ab-initio calculations. Apart from this, the agreement is extremely good, not only for the overall dispersion but also for the intensity distribution. In particular, the bending of the dispersion and the intensity transfer from the acoustic to the optic mode is well reproduced for the TT′ direction. The much more linear dispersion and higher energy reached for the Delta direction is also well accounted for. Looking more into detail, there are some discrepancies, however: The energy difference between acoustic and optical mode along the TT′ direction is larger in the simulation than experimentally observed, and the intensity of the optical mode is somewhat smaller in the simulation. Although the resolution function (which is different for dispersive and non dispersive modes) was not completely accounted for, this certainly points to the limitation of the ab-initio simulation.

3. Molecular dynamics

In the preceeding section, the dynamical structure factor was computed using the eigenvalues of the dynamical matrix. This is not the only method, however. The coherent dynamical structure factor $S_c(q,\omega)$ as measured in an inelastic neutron scattering experiment is actually a correlation function, which can be measured in an MD simulation. More precisely, $S_c(q,\omega)$ is the Fourier transform of the autocorrelation of the coherent intermediate scattering function, given by

$$\begin{aligned}\mathcal{F}^c(q,t) &= \frac{1}{N}\sum_{\alpha,\beta} b_\alpha^c b_\beta^c \left\langle \exp\left(-iq\cdot R_\alpha(0)\right)\exp\left(iq\cdot R_\beta(t)\right)\right\rangle \\ &= \frac{1}{N}\left\langle f(q,0)\overline{f(q,t)}\right\rangle = \frac{1}{N}\left\langle f(q,t_0)\overline{f(q,t+t_0)}\right\rangle_{t_0} \\ f(q,t) &= \sum_\alpha b_\alpha^c \exp\left(-iq\cdot R_\alpha(t)\right), \qquad (2)\end{aligned}$$

where b_α^c is the coherent scattering length of atom α. There exist postprocessing tools [6] which can determine $S(q,\omega)$ directly from an MD trajectory. However, for sufficient resolution in q-space and frequency space a rather large sample and a long trajectory are required, so that the resulting amount of data for the full trajectory cannot be handled. A better way is to compute the spatial Fourier transform already during the simulation, but only for a few hundred q-vectors located on a suitable path in the Brillouin zone. For each of these q-vectors q_i, a time series $f(q_i,t)$ (2) is determined, whose autocorrelation and Fourier transform is then determined in a postprocessing step, using the FFT method [6].

As the linear dimension of the sample is inversely proportional to the resolution in q-space (note that periodic boundary conditions have to be used), rather large samples have to be simulated. Our sample had a size of $167.6\,\text{Å} \times 145.2\,\text{Å} \times 134.1\,\text{Å}$, containing about 200 000 atoms, and was simulated over 160 ps, with a timestep of 2 fs. Such simulations, which were performed with our code IMD [7], are feasible only with classical interaction potentials. For our simulations, potentials of EAM type were used, which had been fitted to reproduce forces, energies and stresses computed ab-initio. This so-called force matching method [8], which is implemented in our potential fitting code *potfit* [9], ensures that even classical potentials make best possible use of quantum mechanical information.

In Fig. 3, the dynamical structure factor is shown in an intensity diagram for the TT′ and Δ directions. $S(q,\omega)$ was rescaled by a factor of $\omega/(n(\omega)+1)$. In this scaling, the acoustic phonon branch would have approximately constant intensity, were it not for the intensity transfer to other branches. In the left plot in Fig. 3, such an intensity transfer to an optic branch is clearly visible. The symbols in the intensity plots mark the location of the peaks in the neutron scattering experiment (cf. Figs. 1 and 2, respectively). Like in the PHONON calculations described

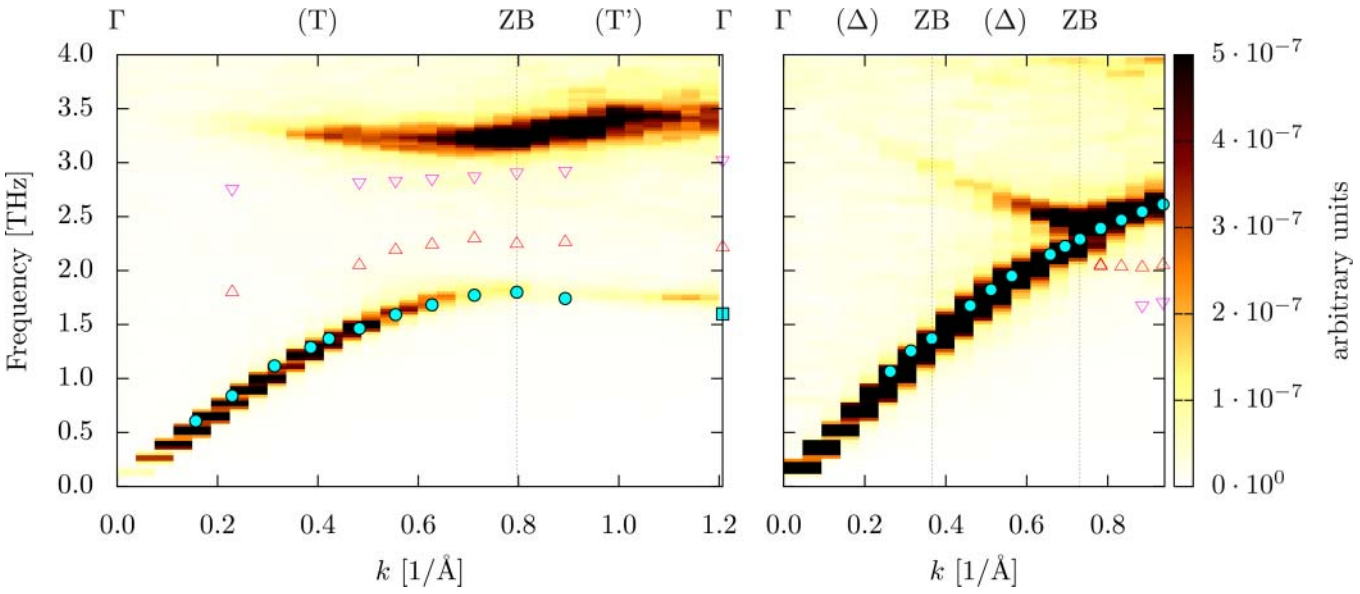

Fig. 3. The scaled dynamical structure factor $S(q,\omega)\cdot\omega/(n(\omega)+1)$ determined from MD simulation is shown for the TT′ (left) and the Δ (right) direction as a color map. The peaks of the neutron intensities (cf. Figs. 1 and 2) are marked as filled circles and open triangles (acoustic and optic branches respectively). The energy axes of the MD results were rescaled by factors of 1.11 (TT′) and 1.21 (Δ), see also text.

above, the energy (frequency) scale of the MD structure factor had to be rescaled by factors of 1.11 and 1.21, respectively – as the potentials were fitted to results from ab-initio calculations, they suffer from the same deficiencies. The factors were chosen to yield an optimal agreement for the acoustic branch. In the TT′ direction, the lower weak optical branch visible in Fig. 1 cannot be seen in the MD intensity plot. The frequency of the upper branch is overestimated slightly, but the intensity transfer to that branch is reproduced reasonably well. In the Δ direction, experiment and MD simulation agree on the almost linear acoustic phonon dispersion relation.

4. Discussion and conclusion

In this paper, we have calculated the dynamical structure factor of $MgZn_2$ with two methods, which both have their advantages and disadvantages. The ab-initio results in harmonic approximation are the most accurate, and show excellent agreement with experiment. Another advantage of that method is the possibility of calculating the eigenvectors, and thus studying in detail the vibrational modes and their relation with the atomic structure of CMA. However, the method disregards all anharmonic effects, and is limited to unit cells of moderate size, so that any effects of disorder cannot be accounted for. The molecular dynamics method, on the other hand, requires classical interaction potentials, and therefore is less accurate a priori. Still, the qualitative agreement with experiment is very good, even if quantitatively the deviations from experiment are somewhat larger than with the ab-initio methods. However, the potential we have used is a preliminary one, and likely can further be improved. The biggest advantage of the MD method is, that it can be used also with very large unit cells, and that it takes anharmonic and disorder effects into account. This will become more important for systems with increasing complexity. We should also stress that the dynamical structure factor, including the intensities, is also a very tough test for any classical potential, which can likely lead to improvements of the potential.

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