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A comparative study of the atomic dynamics of icosahedral ZnMgHo and ZnMgEr by neutron inelastic scattering

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Abstract

The atomic dynamics of the Frank–Kasper type of FI icosahedral alloys ZnMgHo and ZnMgEr have been determined at 200 K using thermal neutron energy loss scattering. From the sum of all double differential scattering cross-sections $d^2\sigma/(d\Omega\ dE)$ weighted with $\sin(\theta)$ the generalised vibrational density of states (GVDOS) was calculated. The calculated GVDOS consists of two bands, a dominant one centered around 20 meV, which is composed of several subbands, and a rather weak one centered around 50 meV. Both alloys show very much the same atomic dynamics with small differences near 15, 22 and 38 meV.

Keywords: Neutron inelastic scattering; Atomic dynamics; Icosahedral alloys

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1. Introduction

Since the discovery of an icosahedral structure in a rapidly solidified Al–Mn alloy [1], much effort has been made to understand the physical properties of this new material. This has encouraged the discovery of many icosahedral quasicrystals in Al-based alloys such as Al-LiCu, AlPdMn, AlCuFe and AlMgZn. Recently, a new icosahedral quasicrystal was reported in ZnMgRe (RE = rare earth) alloy system [2]. This icosahedral system attracts much interest, because these alloys indicated a new combination of elements without Al and transition elements, which are the constituent elements in most of the previous icosahedral alloys. ZnMgRE with 10 to 11 at.% rare earth metals content belong to the most perfect thermodynamically stable icosahedral quasicrystals of Frank–Kasper type existing so far. They are up to now the only family of quasicrystals with localised magnetic moments (due to their 4f-electrons). The localised magnetic moment makes investigations of the magnetic properties of these quasicrystals at low enough temperatures very interesting as others and we have shown earlier [3,4]. But at the same time the strong magnetic neutron scattering rends the atomic dynamics nearly inaccessible. We therefore had to use a special method to be able to finally access the generalised vibrational density of states (GVDOS) and the dynamic structure factor $S(Q,w)$ of $Zn_{65.5}Mg_{22.9}Ho_{11.6}$ and $Zn_{61.4}Mg_{27.7}Er_{11}$. We have performed neutron inelastic scattering (NIS) experiments with the thermal neutron time-of-flight (TOF) spectrometer MARI at the spallation source ISIS, UK, with a sufficiently high incident energy to allow the investigation of the atomic dynamics in a range of momentum transfers where the magnetic form factor is already so small that the magnetic contribution to the scattering could be safely treated as a low, Q-independent 'background'.

2. Sample preparation, characterisation and experiment

The ZnMgHo/Er samples were made in the Crystal and Materials Development Laboratory at the University of Frankfurt by specialist in production of RE/Y containing icosahedral crystals. They were prepared by melting the encapsulated pure elements in a quartz tube in an Ar atmosphere. After melting the sample quartz tube was dropped into water for rapid solidification. Before the experiments, the sample was annealed for 170 h at 550 °C in a sealed quartz tube under Ar. The quasi-crystalline state

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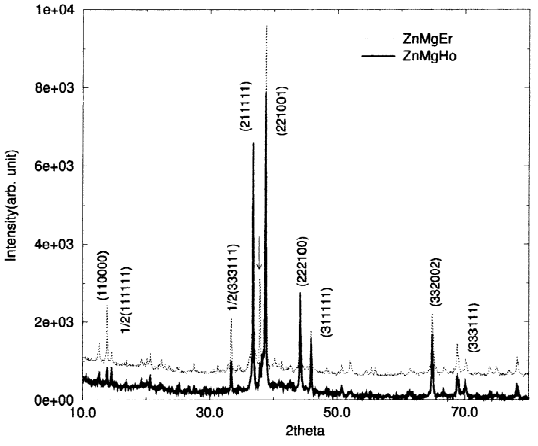

Fig. 1. X-Ray diffraction patterns of the ZnMgHo/Er alloy.

was confirmed by X-ray diffraction using Cu(Kα) radiation and by electron diffraction patterns.

Fig. 1 shows the X-ray diffraction patterns of the ZnMgHo/Er. Almost all peaks can be indexed by a set of icosahedral indices using Elser's method [5]. Icosahedral quasicrystals are often classified into two groups depending on the kind of clusters which dominate their atomic structure. If the cluster structure is dominated by more or less complete Mackay icosahedra, like most of the AlTM (TM = transition metal) i-quasicrystals, the quasi-lattice constant is approximately 0.46 nm and the valence concentration about 1.75 e/a (electron-to-atom ratio). For icosahedral phases of the Frank–Kasper type these values are about 0.52 nm and about 2.1 e/a, respectively. The lattice parameter determined from the (211111) peak (see Ref. [5]):

$$a = \frac{2\pi 13.308}{d_{211111}} \quad (1)$$

is 0.5222 nm. While the valence concentration is found to be 2 (e/a). Thus both entities show that the present icosahedral phase is of the Frank–Kasper type. The diffraction peaks are very sharp, which show a very high ordered quality. The value of the half-width at half-maximum of the (211111) peak is approximately 0.05 nm^{-1}, being smaller than that of about 0.08 nm^{-1} for icosahedral $Al_5Li_3Cu_1$ prepared by the Bridgeman growth method [6]. Also seen in Fig. 1 are the sublattice peaks at 1/2(111111) and 1/2(333111), which indicate the face centred icosahedral phase [7]. Additional weak reflections from a small amount of periodic crystalline phases (mainly Zn_3Mg_7) are detected between the principal peaks (211111) and (221001) especially in the case of one of the two ZnMgEr samples (see Fig. 1), while the second sample had less than 4% foreign crystalline phases. This latter sample made up 80% of the sample used in the experiments. Thus finally we estimated the amount of periodic phases in the sample material used to be of the order of

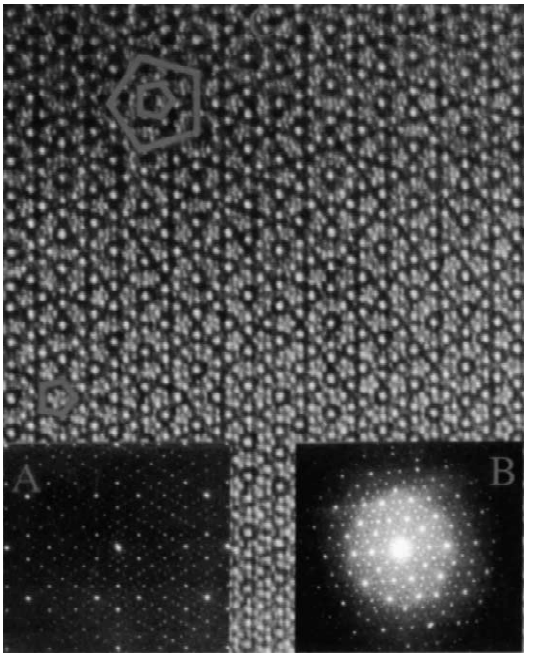

Fig. 2. Electron diffraction patterns taken with the incident beams parallel to the: (A) twofold, (B) fivefold axes, and (C) is the high-resolution image taken along a fivefold axis of i-ZnMgHo alloy.

6%, so that they should hardly affect our spectra. The Insets (A) and (B) in Fig. 2 show the selected-area diffraction patterns of icosahedral ZnMgHo with the incident beams parallel to the twofold and fivefold axes, respectively. Our icosahedral ZnMgEr alloy shows the same diffraction patterns as does the ZnMgHo alloy. The patterns reveal a high density of diffraction spots, including very fine spots as observed in the patterns. We note that the diffraction spots are located very reliably at twofold and fivefold symmetrical positions and do not exhibit distortions. For a more detailed examination, Fig. 2C shows the high-resolution image of ZnMgHo taken with the incident beam parallel to the fivefold axis. Throughout the whole region, the image exhibits a uniform distribution of bright rings (clusters) lying along the fivefold symmetry directions without any distinct shift. One realises that the rings originate from various sizes of pentagons, which can be inflated easily. ZnMgEr shows the same diffraction patterns as ZnMgHo, therefore they are not shown here. Thus, from these structural investigations it is concluded that the samples consist of a face-centred icosahedral phase with very high quality. The experiment was performed with the thermal neutron TOF spectrometer MARI at the neutron spallation source ISIS, UK. An incident energy of 75 meV and scattering angles θ, between 3.4 and 134° were used. The samples and the empty container were measured at 200 K. The calibration run of the spectrometer was done at 200 K with a vanadium spiral of the same size and geometry as the sample. The energy resolution obtained from the full width at half maximum (FWHM) of the

elastic line in the vanadium spectra was 2.7 meV. The 922 TOF spectra recorded were finally summed into 64 spectra from which $S(\theta,w)$ was calculated applying all energy and scattering angle-dependent corrections: background, absorption, detector efficiency and multiple scattering of the neutrons in the sample, except those for the resolution function of the spectrometer.

3. Results and discussion

From the corrected spectra $S(Q,w)$ and (from 1/3 of the spectra at highest scattering angles) the GVDOS were determined. From the bound coherent and incoherent scattering cross section $\sigma^{sc}_{coh} = \Sigma^n_i c_i \sigma^{coh}_i$ and $\sigma^{sc}_{incoh} = \Sigma^n_i c_i \sigma^{incoh}_i$, where c_i is atomic concentration of element i, we can estimate, which kind of vibrations dominate in the spectra. For ZnMgHo σ^{sc}_{coh} and σ^{sc}_{incoh} are 7.554 and 0.157, respectively. For ZnMgEr they are 7.634 and 0.113, respectively. Due to the fact that $\sigma^{sc}_{coh} \gg \sigma^{sc}_{incoh}$ we can preclude that the spectra are mainly determined by collective atomic motions. The measured $S(Q,w)$ is the weighted sum of the partial dynamic structure factors $S_{i,j}(Q,w)$ plus the self part of the structure factors $S^{self}_i(Q,w)$ if the sample scatters neutrons incoherently also:

$$\sigma^{sc} S(Q,w) = 4\pi \sum_i^n \sum_j^n b_i b_j \sqrt{c_i c_j} S_{ij}(Q,w) + \sum_i^n c_i \sigma^{inc}_i S^{self}_i(Q,w) \quad (2)$$

where σ^{sc} is the total scattering cross section, c_i and b_i are the atomic concentration and the bound coherent scattering length for neutron scattering of the element i, respectively. According to Eq. (2) the partial contributions of the three elements to the total dynamic structure factor are given in Table 1 for ZnMgEr and ZnMgHo, respectively.

From this we conclude that the correlations Zn–Zn, Zn–Mg and to more than a factor of four less Zn–Er, Zn–Ho and Mg–Mg contribute dominantly to $S(Q,w)$, while the self-correlations of Zn, Mg, Er and Ho are hardly visible in our case. For most of the elements forming icosahedral alloys the incoherent scattering cross-sections are small [8]. Thus the total dynamic structure factor contains predominantly the information on the collective atomic vibrations.

Table 1
Weighting factors of partial dynamic structure factors of ZnMgEr/Ho

–	$4\pi c_i c_j b_i b_j$	$c_i \sigma^{inc}_i$
–	ZnMgEr/Ho	ZnMgEr/Ho
Zn–Zn	1.5086/1.7129	0.047/0.050
Zn–Mg	0.6483/0.5711	–
Zn–Er	0.3731/–	–
Zn–Ho	–/0.4311	–
Mg–Mg	0.2786/0.1904	0.022/0.018
Mg–Er	0.1603/–	–
Mg–Ho	–/0.1437	–
Er–Er	0.0923/–	0.121/–
Ho–Ho	–/0.1085	–/0.0042

The single particle motions of the atoms are reflected in the generalised vibrational density of states (GVDOS) $G(w)$, which is the normalised weighted sum of the partial vibrational density of states (VDOS) $g_i(w)$ of the element i in the alloy:

$$G(w) = \frac{\sum_{i=1}^{m} e^{-2W_i(Q)} c_i \frac{\sigma^{sc}_i}{M_i} g_i(w)}{\sum_i^m e^{-2W_i(Q)} c_i \frac{\sigma^{sc}_i}{M_i}} \quad (3)$$

Here e^{-2W_i}, c_i, σ^{sc}_i and M_i are the Debye–Waller factor, the atomic concentration, the scattering cross-section and the mass of the element i in the alloy, respectively. Omitting the partial Debye–Waller factors the relative contribution of each element to the measured contribution in ZnMgEr is given by $c_i\sigma_i/M_i$ which is 0.039, 0042 and 0.0057 for Zn, Mg and Er, respectively. Concerning the ZnMgHo alloy $c_i\sigma_i/M_i$ corresponds to 0.041, 0.035 and 0.0057 for Zn, Mg and Ho, respectively. According to these weighting factors the GVDOS determined by NIS is dominated by the vibrations of Zn and Mg with nearly equal weight. The VDOS reflects single particle motions only. For coherently scattering samples one has therefore to remove the interference effects of the collective atomic motions. This can be achieved if the intensity at each energy is sampled in a sufficiently large amount of reciprocal space, so that the variation of the measured intensity with momentum transfer and polarisation vectors averages out in the mean value taken over many Brillouin zones. This can be done by taking the mean value [weighted with $\sin(\theta)$] of the intensity over all accessible scattering angles between the smallest (θ_{min}) and the largest (θ_{max}) for each energy transfer [9,10]:

$$G(w) = \frac{4\pi}{\sigma^{sc}_{coh}} \sqrt{\frac{E_0}{E}} \hbar w (1 - e^{-\beta}) \times \frac{16 m M (E_0 E)^{1/2}}{\hbar^4 (Q^4_{max} - Q^4_{min})} \times \int_{\theta_{min}}^{\theta_{min}} e^{2W(Q)} \left(\frac{d^2\sigma_{coh}}{d\Omega\, dE} \right)_{1phon} \sin(\theta)\, d\theta \quad (4)$$

with E_0, E and m the energies of the neutron before and after scattering and its mass, respectively.

As we had to avoid contributions from magnetic scattering, only scattering angles corresponding to $Q > 80$ nm^{-1} could be used for the investigation of the dynamical properties of the ZnMgRE samples.

In order to determine the phonon density of states, the one phonon part of the double differential scattering cross section has to be separated from the measured intensity, i.e. the multiphonon processes in the measured spectra have to be removed. The calculated multiphonon contributions are subtracted from the measured double differential scattering cross section and this procedure is repeated until

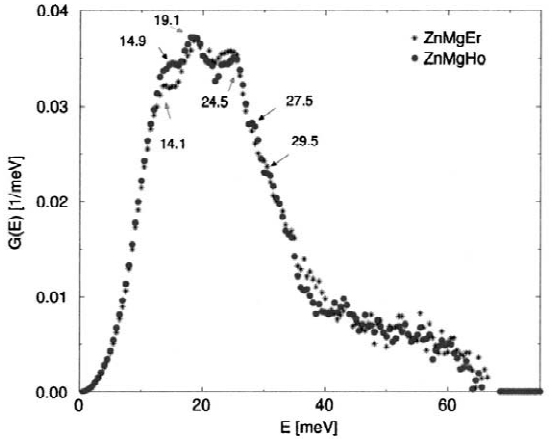

Fig. 3. Generalised vibrational density of states of icosahedral (A) ZnMgEr, (B) ZnMgHo measured at 200 K.

self-consistency is achieved. This method is a reasonable approximation because scattering processes involving several phonons tend to be isotropic like incoherent scattering [10].

Fig. 3 shows the calculated GVDOS of ZnMgEr/Ho, which consists of two bands, a dominant one centered at ca. 20 meV. It is composed of several subbands indicated by shoulders at 14.1, 24.5 and 29.5 meV in the case of ZnMgEr and 14.9, 24.5, 27.5 and 29.5 meV in the case of ZnMgHo. The other band centered around 50 meV is rather weak. Both curves are different from the icosahedral ZnMgY alloy investigated so far [11], as the GVDOS of ZnMgY, with a very similar two-band structure, has a pronounced sharp maximum near 17 meV with two shoulders at 11 and 24 meV. Without assistance from detailed model calculations it cannot be decided which vibrations are the origin of each shoulder or peak observed in Fig. 3, but comparing the intensities with the phonon density of states (PDOS) of the pure elements, it seems reasonable to suggest that the shoulder (subband) found in the frequency distribution of the quasicrystal ZnMgHo/Er around 24 meV could be caused by the Zn atoms, because such a peak was observed in the investigation of the phonon density of states of pure Zn at 24 meV [12] and the Zn–Zn correlations dominate the measured spectra (see Table 1). The second peak around 27 meV is near the principal peak found at 27.5 meV in the investigation of the PDOS of pure Mg [13]. The difference of the GVDOS of ZnMgEr and of ZnMgHo in Fig. 4 shows clearly only small differences in the GVDOS of the two icosahedral samples, except slightly more intensity in the subbands at 22 and at 38 meV in ZnMgEr and in the subband at 15 meV in ZnMgHo.

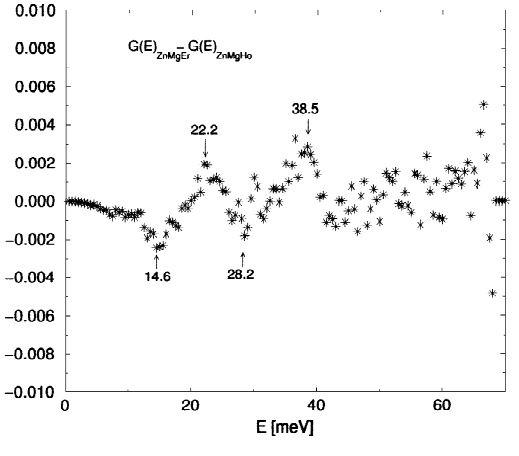

Fig. 4. Difference of GVDOS of ZnMgEr and ZnMgHo measured at 200 K.

4. Conclusion

Compared with each other the i-ZnMgHo and i-ZnMgEr have very much the same atomic dynamic as revealed by this investigation of the GVDOS. The only systematic difference we find is a very slightly higher GVDOS near its maximum near 22 meV and some additional intensity near 38 meV in the case of ZnMgEr with corresponding compensations near 14 and 28 meV. Compared with icosahedral alloys, the structure of which is dominated by Mackay icosahedra, the more detailed structure of the main band seems to be a clear dynamic signature of the Frank–Kasper type of icosahedral alloys.

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