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OF THE LAVES PHASE
INTERMETALLIC COMPOUND CaMg 2

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PHONON SPECTRA
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INTERMETALLIC COMPOUND CaMg$_2$

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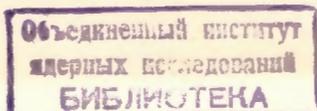
1. Introduction

In a couple of previous papers[1-4],
the phonon spectrum of the Laves phase
compound $MgZn_2$ was investigated theoretically
and experimentally. Interesting features
were found in the calculated dispersion cur-
ves; where for a close-packed structures
unusually low-lying rotational modes appea-
red with a tendency to go soft as the tempe-
rature decreases. An interpretation was given
in terms of peculiarities of the C-14 struc-
ture of this substance[2]. Despite an exten-
sive search these modes could not be detected
experimentally in an energy range up to about
10 meV, and it still remains an open questi-
on, why.

Unfortunately, the model pseudopotenti-
al of Zn is not very precisely known[5,6] and
it is difficult to get satisfactory agree-
ment between measured and calculated phonon
dispersion curves even for pure Zn. There-
fore, one feels uncertain about the theore-
tical results for $MgZn_2$ (though the low-
lying rotational modes turned out to be very
insensitive to changes of the potentials).

In this situation it is desirable to
include into consideration another substance ,

where the potential is more reliable. Only very few compounds of C-14 structure exist, where both constituents are pseudopotential metals. We have chosen $CaMg_2$. Magnesium is one of the best pseudopotential materials. For application of pseudopotentials to Ca see[7]. In fact, we got quite encouraging results for the slope of the acoustic modes as compared with the measured elastic constants.

But now difficulties arise at the preparative step and no single crystals were available for us. We decided to determine the phonon density of states by coherent inelastic neutron scattering on a polycrystalline sample[8,3]. Unfortunately, in the end the sample material contained about 0.3 to 1 at .% water which completely masked the results at energies higher than 15 meV. However, the results in the lower energy range are in satisfactory agreement with the calculated ones.

Though $CaMg_2$ and $MgZn_2$ have the same structure, there are important differences between the two substances which are manifested in the phonon spectrum. The main difference is that the mass ratio between A and B atoms (in the notation A_2B for the compound) is reversed in $CaMg_2$ as compared with $MgZn_2$. Note that the A-type atom (Mg) of $CaMg_2$ is almost three times lighter than the A-type atom (Zn) of $MgZn_2$. This causes an upwards shift of the frequencies of all modes where the A atoms dominate in comparison with frequencies of those where the B atoms dominate. For this reason, the calculated phonon density of states of $CaMg_2$ greatly differs from that of $MgZn_2$. Especially the above-mentioned

rotational modes in which only A atoms vibrate appear in $CaMg_2$ at appreciably higher frequencies and no soft mode behaviour is observed in their temperature dependence calculated with the quasi-harmonic approximation.

We proceed now in Section 2 with the explanation of the details of the calculation and presenting the results. In Section 3 the measurements are reported. In order to check the reliability of the density of states results determined from coherent neutron scattering we made a full calculation[9] of the neutron scattering cross section averaged over the scattering angle range used in the experiment. The results are discussed in Section 4.

2. Pseudopotential Calculation

The method of calculation is completely analogous to that reported in [2], that is, second-order perturbation theory[11]. For details of the structure and of the symmetry of vibrational modes see[1,2]. The lattice parameters at room temperature are[10]

$$a = 11.78 \text{ a.u.} \quad c = 19.12 \text{ a.u.}$$

As in ref.[1,2], we used the ideal values for the parameters x and z of the structure, since there is no experimental evidence of any deviation.

The non-local and energy-dependent Shaw model pseudopotential[5] was used, the parameters of which are given in the Table.

Table

Parameters of the Shaw Potential

	$A_0(E_F)$	$\frac{dA_0}{dE}E_F$	$A_1(E_F)$	$\frac{dA_1}{dE}E_F$	Z
Ca	0.570	−0.388	0.605	−0.110	2.393
Mg	0.785	−0.286	0.914	−0.058	2.139

They were obtained assuming the core shifts being the same as in the pure metals[12]. The screening function of Singwi et al.[13] was used in the calculation of the energy-wave-number characteristics. The elements of the dynamical matrix were computed by summing up over about 1500 reciprocal lattice vectors. The convergency was checked to give a 0.5% accuracy for all frequencies.

The calculated dispersion curves on symmetry lines are shown in Fig.1. The slope of the acoustic branches, calculated from the experimental elastic constants[14]

$$c_{11} = 6.124 \cdot 10^{10} \text{N/m}^2 \qquad c_{33} = 6.552 \cdot 10^{10} \text{N/m}^2$$

$$c_{44} = 1.927 \cdot 10^{10} \text{N/m}^2 \qquad c_{12} = 1.76 \cdot 10^{10} \text{N/m}^2$$

$$c_{13} = 1.5 \cdot 10^{10} \text{N/m}^2$$

is also indicated in Fig.1. The agreement is quite satisfactory regarding the fact that the calculation contains no adjusted parameters.

Note that the rotational modes discussed in the Introduction (the 3rd and 4th optical branch at point Γ) now appear at
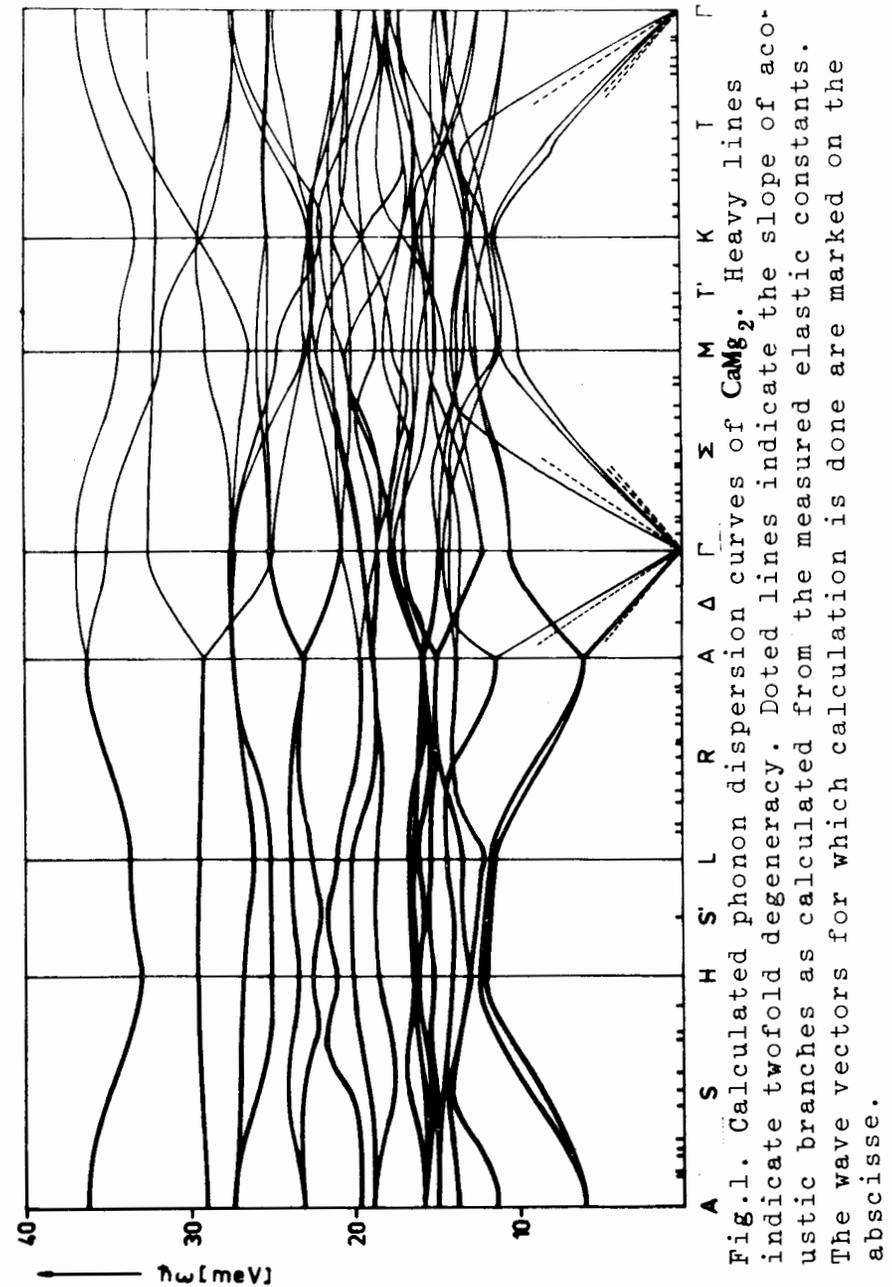

Fig.1. Calculated phonon dispersion curves of CaMg$_2$. Heavy lines indicate twofold degeneracy. Doted lines indicate the slope of acoustic branches as calculated from the measured elastic constants. The wave vectors for which calculation is done are marked on the abscisse.
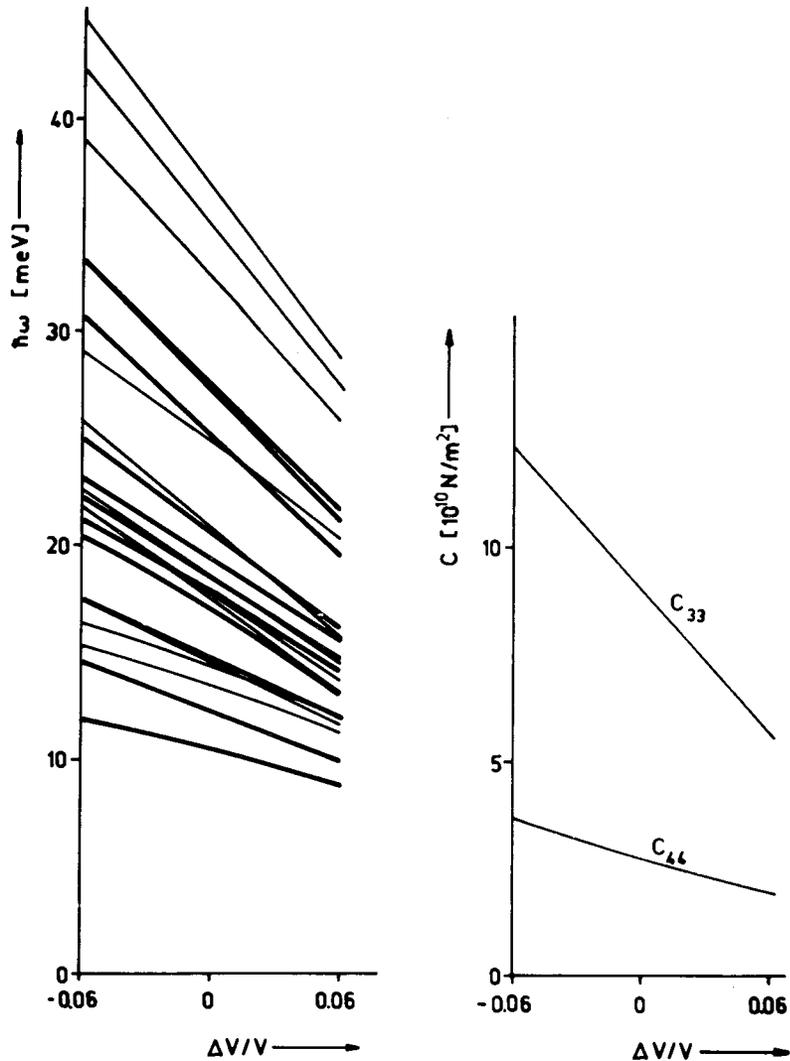
Fig.2. Volume (i.e., temperature or pres-
sure) dependence of the phonon frequencies
at point Γ and of the elastic constants as
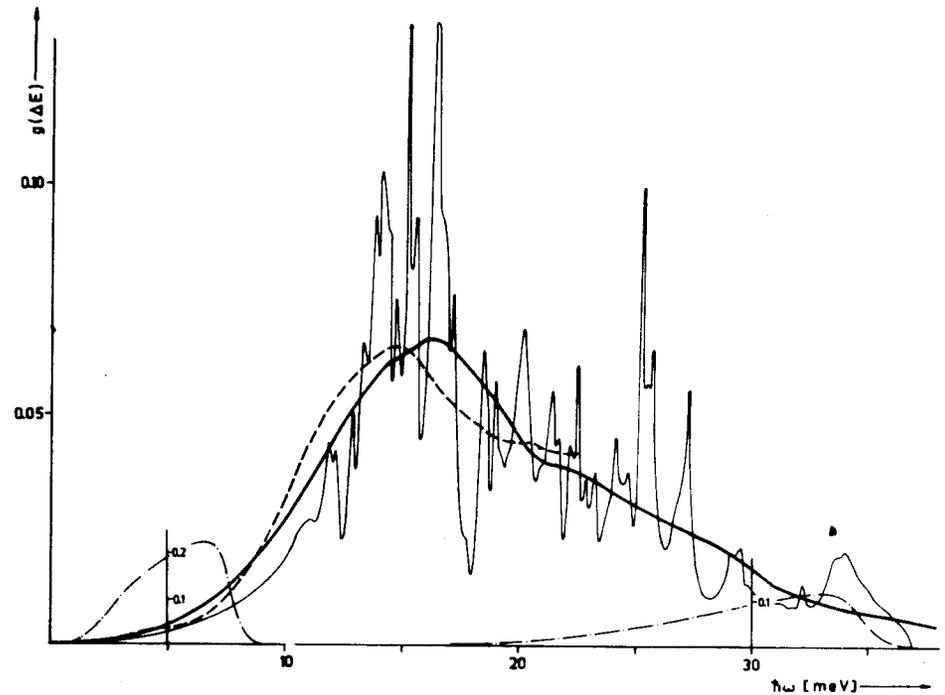calculated from the quasiharmonic approxi-
mation.

Fig.3. Light line - calculated phonon density
of states, heavy line - the same folded with
the resolution function of the spectrometer
used in the experiment dot-dashed line -
resolution function for two energies dashed
line - measured phonon density of states.

about 14 meV (cf. with 3 meV in $MgZn_2$). They
also do not show any anomalous temperature
dependence if calculated in the quasiharmo-
nic approximation, neither do the elastic
constants (Fig.2).

The phonon frequencies and polarization
vectors were also calculated on a regular
lattice of 76 equidistant points in the irre-

ducible part of the Brillouin zone and from these data the phonon density of states was calculated using the tetrahedron method[15]. The results are shown in Fig.3. Again as in the case of $MgZn_2$ [2] we get a rapidly oscillating curve due to the many interacting branches, but the general shape is quite different as is discussed in the Introduction. We folded this curve with the resolution function of the spectrometer used in the measurement (next section) and compared the result with the experimental one as is also shown in Fig.3. The agreement is again satisfactory. The about 10% shift of the calculated values to higher frequencies coincides with the results obtained for the elastic constants (Fig.1).

3. Experimental

The measurements of the spectra of inelastically scattered neutrons on $CaMg_2$ were performed on a time-of-flight spectrometer with a nitrogen cooled beryllium filter in front of the detector (inverted geometry)[16,20] at the pulsed reactor in Dubna[17]. The neutrons of the white beam are down scattered. For the energy analysis neutrons with mean energy of 4.08 meV were used. The collimation is rather poor. The angle divergency depends on scattering angle. It varies from about 5 to 7 degrees halfwidth of the angle dependent detection function. The channel width of the time analyser was 32 μsec. The flight path between the moderator and the sample was about 32 m and between the sample and the detector 1.25 m/sinϕ (ϕ -scattering angle). In connection with the reactor pulse

width of about 100 μsec this gives a time resolution (halfwidth of a very asymmetric function) of about 12% to 7% for an energy transfer of 10 meV to 50 meV, respectively[18,20].

Polycrystalline $CaMg_2$ was used for preparing the sample about 5 mm thick and 180 mm in diameter. During the measurements the sample was kept in an evacuated volume, since $CaMg_2$ is hygroscopic. The TOF-spectra of $CaMg_2$ are measured at room temperature for scattering angles of 75°,90°,105°,120° and 135° (Fig.4). The shown spectra are cor-
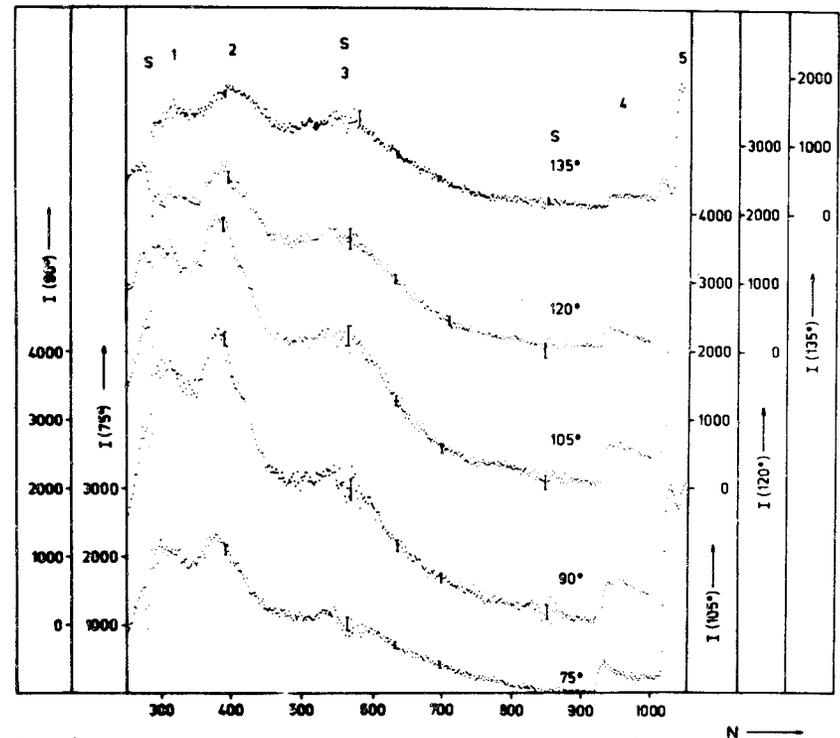

Fig.4. Time-of-flight spectra of inelastically scattered neutrons on $CaMg_2$ and different scattering angles 75°,90°,105°,120° and 135° (I-intensity, N-channel number).

rected for the background and the so-called satellites as described in [21] . Energy regions covered by the satellites are marked with S. In these ranges the errors are larger. High energy peaks (1 and 2 in Fig.4) should be caused by water, which is connected with the hygroscopic sample $CaMg_2$. The amount of water in $CaMg_2$ was estimated by comparing peak intensities in the TOF-spectra to be less than 1 at.%. The energies of these maxima are about 70 meV and 40 meV, respectively. The maximum 3 corresponds to phonons in $CaMg_2$ and the cut-offs marked by 4 and 5 to the beryllium cut-offs (002) and (100), respectively.

In [19] it is shown that the water peak moves to lower energies if it is adsorbed on matter. So the 70 meV of the rotational peak of free water shouldn't be in contradiction with our results. The curve in [19] for adsorbed water is fitted to our peak 2 in Fig.4 and subtracted from it. Of course, the precision of this procedure is rather poor.

Since the low energy part of the water curve is smooth, the corrected TOF-spectra of $CaMg_2$ will reflect the main features of the true spectra in the energy range up to about 15 meV. The higher energetic parts remain very uncertain.

The so-corrected spectra corresponding to different scattering angles have been normalized mutually. In the following the results were handled with respect to the proposal of Bredov et al. [8] to calculate the phonon density of states. The result is shown in Fig.3. The accuracy of the method for the non-cubic intermetallic phase $CaMg_2$ has been investigated as described in the
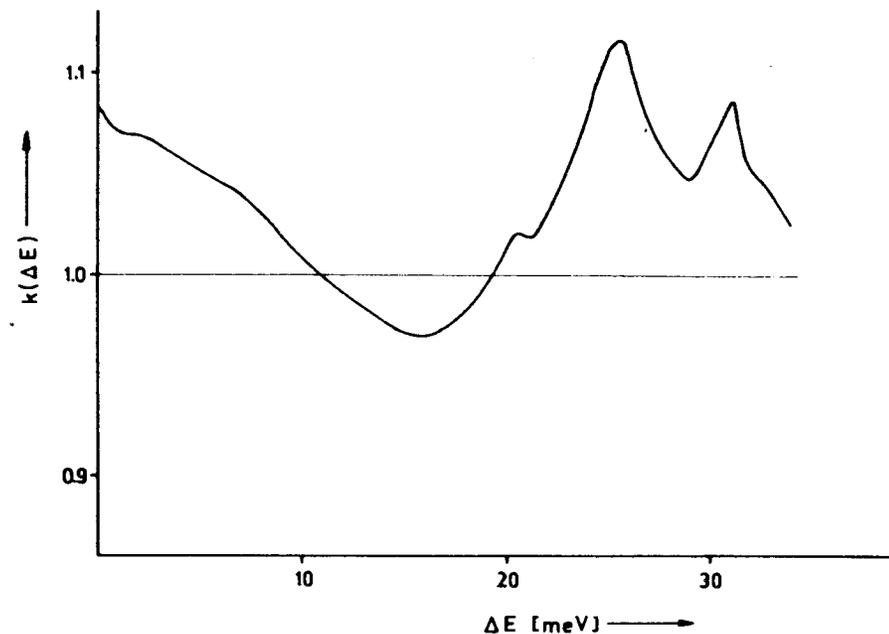

Fig.5. Coherency effects in the density of states measurement [9]. Due to coherency effects, the quantity $Q(\Delta E) = k(\Delta E) g(\Delta E)$ is measured instead of the phonon density of states $g(\Delta E)$.

next Section leading to a maximal error of 12%.

4. Check of the Experimental Method

Because energy and momentum are conserved in the coherent scattering process on phonons, the coherent scattering usually does not give the phonon density of states. The phonon density is only approximately obtained after the averaging over a large range of scattering angles and over all crystal orientations (polycrystalline

sample)[8] . The accuracy hereby depends on the used range of scattering angles and on properties of the sample material (mainly the structure). The only certain way to estimate the accuracy is to calculate the scattering cross section from the calculated phonon spectra and to compare it with the calculated density of states. We made a full calculation, the details of which are discussed in [9] . The relative error of the measurement of the density of states due to coherency effects is given by the deviation of the function $k(\Delta E)$ of [9] from unity. This function calculated for $CaMg_2$ is shown in Fig.5. The only difference with [9] is that here the angular dependend Debye-Waller factor was calculated for each atom and taken into account in the cross section calculation. The results show that coherency effects are less than 10%.

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