Measurements

For sample preparation powder fractions of about 90 μm particle size were spread between two microscope cover slides, held apart at a distance of 0.4 mm by a metal spacer. All measurements were made with reference to a quartz powder sample. Because of the high refractive index of CdI₃P₄S₂2(12), index-matching liquids could not be used. The increased SHG intensity of CdI₃P₄S₂2(12) as compared with CdI₄P₄S₂4 may be explained by the presence of the highly polarizable I⁻ ions in the anionic sublattice.

Kurtz & Perry (1968) have shown that the shapes of the curves displaying relative SHG intensities of powders vs the ratio particle size/coherence length differ drastically for phase-matchable and non-phase-matchable materials (Kurtz & Perry, 1968). Fig. 3 shows measurements of SHG intensities vs particle sizes for CdI₃P₄S₂2(12) (Cc) and CdI₄P₄S₂4 (Cc).

An exact answer to the question whether the materials are phase-matchable or not can only be given if the coherence lengths are known. Unfortunately, single crystals of sufficient size for the coherence lengths to be measured could not yet be prepared. In common SHG materials, however, coherence lengths are of the order of magnitude 1–10 μm; thus, from the shape of the curves in Fig. 3 it can be inferred with high probability that these materials are phase-matchable for 1060 nm.

Summary and conclusions

Our measurements of SHG in powders of several, icosahedral compounds showed that this family of materials, comprising a wide range of chemical compositions and allowing a large variety of substitutions, may be a potential source for new, non-linear optical materials. The highest SHG effect, comparable with that in powders of LiNbO₃, was detected in the monoclinic compound CdI₃P₄S₂2(12). This material is likely to be phase-matchable at 1060 nm. Experiments to grow single crystals are under way.

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References


Evidence of non-cubic lattice distortions around vacant sites in Co–Ga β' phases. By G. KIRCHGRABER and V. GEROLD, Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, and Institut für Metallkunde, Universität Stuttgart, Federal Republic of Germany

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Diffuse X-ray diffraction from Co–Ga single crystals containing 48 to 56 at.% Co gives evidence for strong distortion fields around vacant sites in the Co sublattice and less strong fields around Co atoms on the Ga sublattice. The distortion is comparable to that occurring in Zr–20 wt.% Nb alloys and is characterized by shifts of atoms parallel to <111>. The distortion has some similarity to the atomic structure of the α phase found in Zr–10 wt % Nb.

Introduction

In an attempt to investigate the local order defect structure in the ordered β' phase of Co–Ga, diffuse X-ray experiments from single crystals were undertaken using monochromatic Mo Kα radiation. The diffraction pattern showed unusually strong intensity maxima in the background scattering which could only be explained by the occurrence of relatively
strong lattice distortions. Short-range order would give only minor intense peaks caused by some ordering of lattice defects in the otherwise strictly ordered phase. The types of possible point defects are: (a) a Co atom on a Ga sublattice site and (b) a vacancy on a Co sublattice site. The concentration of each defect depends highly on the composition and on the heat treatment of the alloy, as has been reported earlier (Berner, Geibel, Gerold & Wachtel, 1975; Berner, 1976). The purpose of this paper is to present these preliminary results and to compare them with experimental results on Zr–Nb alloys (Lin, Spalt & Batterman, 1976) and to a model calculation by Kuan & Sass (1976).

Experimental results

Single crystals of Co–Ga were prepared with the Co content listed in Table 1. From these specimens, flat samples with (111) surfaces were spark cut. These specimens were annealed at 900°C in evacuated quartz tubes and rapidly cooled to room temperature by plunging the tubes into water without breaking them. After measurement of the diffuse scattering for the ‘as-quenched’ condition in the [hkl] and [hkl±h] directions of the reciprocal lattice, the slices were annealed at 600°C for 72 h to attain thermal equilibrium at that temperature (Berner, 1976). After cooling the samples to room temperature, the diffraction experiments were repeated.

All experiments are listed in Table 1, together with the concentrations of the vacant sites $c_v$ and of the wrongly positioned Co atoms $c_{TB}$ taken from Berner et al. (1975). Fig. 1 shows the observed intensity distribution along the [hkl] direction for experiments 2 and 8 in Table 1. Besides the matrix 222 and 444 and the superstructure reflections [hkl] and [hkl±h], respectively, designated as A, B and C. The peaks A and C from experiment 8 are substantially higher than for experiment 2, whereas peak B shows little variation. In the [hkl±h] direction, one observes the matrix peak 223 and peaks arising from tails of the close-by matrix peaks 112 and 334. In addition, there is another broad peak centered at $\frac{2}{3},\frac{1}{3},\frac{1}{3}$ designated as peak D.

The intensities have been measured in absolute units, i.e. in multiples of the square of the average atomic scattering amplitude, $(f)^2$. The peak heights (after subtraction of the background) are listed in Table 1, with the exception of peak B. This peak did not vary with heat treatment and composition.

Discussion of the results

In spite of the fact that the experiments reported are so far limited to only two directions in the reciprocal lattice, the similarities to the work by Lin et al. (1976) on Zr containing 20 or 30% Nb are striking. These authors reported the intensity distribution in the hhl plane of the reciprocal lattice. They found diffuse peaks elongated in the [112] direction at positions shifted by (112)/3 from the matrix peaks HHL.* These peaks corresponds to peaks A, B and D of the present work, whereas peak C is only a saddle point of an intensity streak connecting matrix peak 332 with the elongated peak D. The intensity of the elongated peaks increases with distance in the [111] direction.

Besides these similarities there exist also differences. Compared with Zr–20% Nb, and even Zr–30% Nb, the normalized intensities for Co–Ga are always smaller. In Table 2 the largest peaks of the present experiments (experiment 8) are compared with the intensities from both Zr–Nb alloys. In addition, the small shifts of the peaks from their ideal positions as observed in Zr–Nb were not found for Co–Ga.

![Fig. 1. Two diffraction curves along the line hhh in reciprocal space (experiments 2 and 8 from Table 1) showing diffuse peaks A, B, and C.](image)

Table 2. Comparison of peak intensity data from CoGa (experiment 8), Zr–20% Nb and Zr–30% Nb

The Zr–Nb data are extrapolated from the corresponding figures [3] and are only approximate.

<table>
<thead>
<tr>
<th>Peak</th>
<th>CoGa experiment 8</th>
<th>Zr–20% Nb</th>
<th>Zr–30% Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.0</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>1.7</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>D</td>
<td>1.7</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

Recently, preliminary results have been reported by Georgopoulos & Cohen (1977) on diffuse scattering from

* For positive $H$. For negative $H$, the direction is reversed. There exists also a second set of peaks elongated and shifted in the [112] direction.

Table 1. Details of the experiments

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Cobalt concentration at.%</th>
<th>Temperature °C</th>
<th>Defect concentration $c_v$ at.%</th>
<th>Absolute peak intensities measured in units of $(f)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>56</td>
<td>600</td>
<td>0</td>
<td>0.17 0.17 0.51</td>
</tr>
<tr>
<td>2</td>
<td>53</td>
<td>600</td>
<td>1.1</td>
<td>3.65 0.206 0.54</td>
</tr>
<tr>
<td>3</td>
<td>50.2</td>
<td>600</td>
<td>2.4</td>
<td>1.4 0.294 0.72</td>
</tr>
<tr>
<td>4</td>
<td>49</td>
<td>600</td>
<td>3.0</td>
<td>0.43 0.46 1.03</td>
</tr>
<tr>
<td>5</td>
<td>53</td>
<td>900</td>
<td>3.3</td>
<td>4.75 0.515 1.14</td>
</tr>
<tr>
<td>6</td>
<td>48</td>
<td>600</td>
<td>4.2</td>
<td>0.1 0.46 0.94</td>
</tr>
<tr>
<td>7</td>
<td>49</td>
<td>900</td>
<td>4.9</td>
<td>1.45 0.70 1.54</td>
</tr>
<tr>
<td>8</td>
<td>48</td>
<td>900</td>
<td>6.2</td>
<td>1.1 1.03 1.72</td>
</tr>
</tbody>
</table>
\(\beta\)-phase Ni–Al single crystals which show a similar defect structure. They observed a peak corresponding to peak \(A\) and claimed that the peak intensity increases with increasing concentration of either or both defect types. For this reason an attempt was made to analyze the present data based on the assumption that both defects are contributing to the peak intensity in the following way:

\[ I_n = a_n + b_n(c_v + c_T B), \]  

where \(n\) is the index of the peak (\(A, C\) or \(D\)) and \(a_n, b_n\) and \(c_v\) are unknown constants which are determined by a least-squares fitting to the experimental measurements. The results are plotted in Fig. 2 for peaks \(A\) and \(C\) and in Fig. 3 for peak \(D\). In the first two cases, \(\alpha\) was found to be \(0.17\), whereas for peak \(D\) the \(\alpha\) value was \(0.21\). Thus it can be concluded that the vacant site on the Co sublattice is contributing much more to the peak intensity than the wrongly positioned Co atom.

The observed peaks can be explained by atomic shifts around the point defects with a strong component in one of the four \(\langle111\rangle\) directions. This follows from the peak ratios in Fig. 1. The peak positions suggest a complex distortion where the \(\langle111\rangle\) shifts occur in opposite directions for neighboring \(\{111\}\) planes in a similar way to that known from \(\omega\) transformations or from \(\omega\)-like lattice distortions which seem to be present in the reported Zr–Nb alloys.

Recently, Kuan & Sass (1976) reported a similar atomic model to explain the neutron diffraction observed from Zr–20\% Nb by Keating & La Placa (1974). These experiments are restricted to a smaller range in the reciprocal lattice than those by Lin et al. (1976). Kuan & Sass (1976) claim that only a model based on displacements centered about a lattice vacancy can account for the observed peak shifts. In such models the peak intensities are given by

\[ I_n = I_n^v c_v / 4, \]  

where \(I_n^v\) is the intensity of peak \(n\) calculated from a single defect. The factor \(\frac{1}{4}\) results from the fact that four defect orientations exist, but only one of them contributes to peak \(n\). As an example, the Kuan–Sass model gives for peak \(A\) a value \(I_n^v = 1200(f)^2\). It should be mentioned that the model would need a vacancy concentration of about 1\% to explain the absolute intensity measurements of Lin et al. (1976). This seems to be a very high value for the Zr–Nb alloy, a fact which has not been established by other means.

In the case of Co–Ga, the dependence of peak \(A\) intensity on vacancy concentration has been proved. If one neglects the possible small contribution from other defects, a vacancy distortion model needs only an intensity \(I_n^v = 67(f)^2\), which is smaller by a factor of 20 than that of the Kuan–Sass model. Compared with the monotonic Laue scattering induced by randomly distributed vacancies, this value is still 16 times larger. If one takes the relatively low concentration of vacancies into account, the possible contribution of short-range order to the peaks is very small and can be neglected.

In conclusion, these preliminary experiments on Co–Ga alloys have demonstrated that the observed diffraction peaks can be largely explained by \(\omega\)-like distortion fields around vacant sites. A distortion model similar to that proposed by Kuan & Sass (1976) may be valid, but the total distortion is expected to be much smaller. Further experiments and model calculations are in progress, which may give more precise information.

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References