LOW TEMPERATURE X-RAY DIFFRACTION ANALYSIS OF THE LATTICE DISTORTION AND THE STRUCTURE OF CRYSTALS IN CONNECTION WITH MAGNETIC ORDERING

THESIS

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SUMMARY

In this work, a high precision X-ray diffraction measurements, in connection with an accurate peak profile analysis, was used in order to find out whether there is a crystallographic phase transition in the rare earth tetraborides; ErB_4 and TbB_4 at low temperatures.

Variable temperature X-ray diffraction measurements were performed for ErB_4 and TbB_4 on the CGR-diffractometer which was especially adjusted in the present work in order to fulfil the optimum accuracy needed in this type of work. The diffractometer setting was optimized for maximum angular resolution applying a NBS-Si standard sample and Cu-K_α radiation with a pyrolythic graphite monochromator. The temperature settings were controlled automatically by a cryogenics temperature controller together with an accessory flow control panel for cold liquid. Temperature stability during measurements was ±0.5 K measured by iron-gold against chromel thermocouple. The reproducibility of the experimental conditions and the accuracy of the analysed profile data were tested in different measurements on some standard materials : Si, SiO_2 and Al_2O_3.

Total profiles of selected reflections for ErB_4 and TbB_4 were measured in the step-scanning mode ($\Delta 2\theta = 0.01°$) at a number of constant temperatures starting at 300 K and ending at 4.2 K. Lattice distortions were studied by individual peak profile analysis for the selected reflections.

A special program for profile fitting called (PROFIT) was suggested and designed to extract all the informations needed when applied in profile analysis of all sort of peaks and for covering a wide range of angles. A comparison of the performance of different profile shape functions in representing X-ray peak profile, was executed. Also, the different models suggested for profile asymmetry were intercompared in fitting low and high asymmetry profiles.

Complete X-ray diffraction measurements were taken at room temperature on PW050 Philips diffractometer for $Ho(Fe_x Al_{1-x})_2$, ErB_4 and TbB_4. The diffraction diagrams of these compounds together with that of the standard materials represent variety of data kinds. A profile fitting for the resulting diffraction diagrams was performed. Then, the resulting profile parameters were used for calculating and refining crystal structure parameters by applying the least-squares programs POWLS and FINAX. The validity of the present profile fitting procedure was estimated by comparing the resulting structure parameters of these compounds with the corresponding values from the literatures.

Very accurate evaluations and examinations of the results obtained, based on the best reliability factor, led to some important findings that can be used in different profile modelings. The main results obtained can be summarized as follows :

1) Among the four functions: Gaussian, Lorentzian, Pseudo-Voigt and pearson VII, the Gaussian was consistently the worst performer in representing X-ray powder profile, while the Pseudo-Voigt and Pearson VII were the best and gave more or less the same results. For the present application of phase transition, the Pearson VII was preferred because its shape parameter gives direct indication about the profile shape and the non-necessity of good initial values.

2) For asymmetry in profiles, the separate fitting of left and right parts of the profile was the best model among the proposed ones. This model was found to be efficient in the diffraction range $20° < 2\theta < 135°$.

3) The assumption of identical profiles for $K_{\alpha 1} - _{\alpha 2}$ peaks was found to be an approximation that yields higher reliability factors.

4) Excellent reliability factors were obtained for the profile fitting of $Ho(Fe_xAl_{1-x})_2$, ErB_4 and TbB_4 at room-temperature. The comparison between the structure parameters of these compounds based on profile parameters from PROFIT program, and the corresponding values from literatures showed the validity of the present profile fitting technique in dealing with variety of data types. The combined experimental and analytical procedure was suitable to identify fractional changes ($\Delta a/a$) in the lattice parameters as low as 2.10^{-5}.

5) The isostructural rare earth tetraborides ErB_4 and TbB_4 of tetragonal space group P4/mbm, were found to undergo crystallographic phase transitions to orthorhombic symmetry. This

tetragonal/orthorhombic distortions were discussed in correlation to the antiferromagnetic phase transitions of ErB_4 at $T_N = 13$ K and of TbB_4 at $T_N = 43$ K. The causal interference between structural and magnetic phase transitions differs between the two compounds.

a) In TbB_4 :

i) The structural phase transition occured at a definitely higher temperature, T = 80 K, than the magnetic ordering temperature $T_N = 43$ K. Accordingly, two separate (second order) phase transitions were stated for TbB_4.

ii) The thermal contraction of the tetragonal lattice parameter (a) was about 0.003 Å going from 300 to 80 K, whereas for the (c) parameter no thermal variation could be observed within the error margins of 0.0003 Å.

iii) The temperature dependence of the lattice parameters showed a symmetrical splitting of the tetragonal a-axis into orthorhombic a and b-axes with a difference between (a) and (b) of 0.020(4) Å at 4.2 K.

iv) The unit cell volume was nearly unaffected during the phase transition. The relative volume change between 300 and 4.2 K was less than 10^{-3}.

v) The phase transition was assumed to be driven by a strong electron-lattice coupling or by an electronic quadrupole-quadrupole interaction between the Tb ions.

b) In ErB_4 :

i) The tetragonal/orthorhombic lattice distortion occured simultaneously with the antiferromagnetic ordering around T_N = 13 K. Therefore, only one phase transition was stated for ErB_4.

ii) The thermal contraction of the tetragonal lattice parameter (a) was linear and equal to about 0.004 Å going from 300 K to the orthorhombic transition below 15 K. For the c-axis, a continuous decrease of about 0.003 Å was observed going from 300 K to 4.2 K.

iii) The temperature dependence of the lattice parameters showed a rather small splitting into orthorhombic (a) and (b) below T = 15 K. The difference between (a) and (b) was smaller than 0.003 Å while the significant limit for the accuracy of the data was just 0.003 Å.

iv) The relative volume contraction of the unit cell was 2.3×10^{-3} from 200.48(2) $Å^3$ at 300 K to 200.04(4) $Å^3$ at 4.2 K.

v) The lattice distortion was attributed to magnetostrictive effects during the magnetic ordering process, where the structural symmetry was adapted to the orthorhombic magnetic moment configuration.

6) The present findings of low temperature phase transitions from tetragonal to orthorhombic symmetry eliminate the discrepancy existing so far between the symmetry of the antiferromagnetic structure of the ordered moments (orthorhombic), and the symmetry of the crystallographic unit cell (tetragonal).

CHAPTER I

INTRODUCTION

In qualitative and quantitative X-ray diffraction problems, overlapping profiles introduce difficulties that prevent an accurate determination of profile's parameters for the diffraction lines. Moreover, even if the peaks are separated from each other, the accuracy in the profile's parameters, derived by conventional methods, is poor because of the instrumental effects and limited angular resolution; the step-width is normally $\Delta 2\theta = 0.01°$. Therefore, the profile analysis technique is essential for most applications such as structure refinements, phase identification, indexing of unknowns and critical phase transitions. With the help of profile fitting very precise parameters that define position, shape, width and height of each diffraction line can be determined. For some problems which involves critical phase transition, the profile analysis is, sometimes, the only way to detect such transitions. The profile analysis becomes nowadays the backbone for a proper data evaluation of powder diffractometry.

In treating with magnetic materials, the neutron diffraction is used for studying the magnetic properties and magnetic structure of such materials. Neutrons interact with the nuclei of the atoms in the material, and at the same time there is a dipole-dipole interaction between the magnetic moment of the neutron and that of the magnetic atoms. X-ray diffraction is based on electromagnetic interaction, and hence it is not preferred for studying the magnetic materials. But due to the poor angular resolution of neutron diffraction, it can not, usually, detect the small distortions in a crystal structure. Therefore, parallel X-ray measurements are needed to study the behaviour of the crystal structure during the magnetic ordering investigations for magnetic materials.

1.1. CLASSIFICATION OF PHASE TRANSITIONS :

The features of different kinds of transitions are summarised in *Helen [1]* classification scheme. Only transitions involving no change of chemical compositions are considered, where a single-phase material changes into another single phase material of the same composition. The distinctions down are not completely sharp, but it can serve as a guide. These classifications are listed below :

(1) **Reconstructive** : no orientation relationships; complete fragmentation of single crystals.

(2) **Substitutional order-disorder** : close orientation relationships; interchange of atoms, randomly, by diffusion.

(3) **Martensitic** : coars orientation relationships, with large change of shape; no diffusion.

(4) **Reversible** : close orientation relationships; changes reversible in single crystal; changes of atomic positions rather small, with reversible path :

(i) Pure displacive : no breaking of bonds; topology completely unchanged.

(ii) Hydrogen-hopping : order-disorder changes of hydrogen atom in a bond; small displacements of other atoms.

(iii) Orientation-switching : order-disorder changes of orientation of small groups of atoms; small displacements of other atoms.

(iv) Order-disorder changes of intra-atomic state.

(v) Jahn-Teller changes.

A reconstructive transition is characterized macroscopically by its sluggishness and by the irregular orientation of crystallites of the new phase, and structurally by large changes in the topology of the linkage. The criterion for a displacive transition is that the new structure should be capable of being derived from the old by a continuous and ordered process of atomic displacement. The largest displacements being so small that no bonds involved in the cohesion of the structure are broken. The path from one structure to the other is reversible for individual atoms. Though reconstructive transitions involve more obvious changes than do displacive, it is probably true that they are of less common occurrence.

Substitutional order-disorder transitions resemble both; reconstructive and displacive transitions. They differ from both in having a finite temperature interval from the first onset of disorder to its completion. Martensitic transitions resemble displacive transitions in that the process can be followed as a continuous concerted movements of atoms from the old positions to the new, but differ in the size of the displacements, which are so large that the environments of all, or most, of the atoms are changed in the process. Moreover, they are generally not reversible on the atomic scale and the original single crystal is not reformed.

Both; the hydrogen-hopping transitions and the orientation-switching ones can be thought of as displacive transitions to which a particular localised geometrical disordering has been added, organised in small domains. The category 4(iv) comprises transitions which are pure displacive as far as the position of atomic centres is concerned, but the displacements are a consequence of ordering of the internal state of the atoms. They include transitions due to ordering of valency electrons or due to ordering of magnetic spins. The interatomic forces due to the set of ordered magnetic spins are additional to the ordinary structural forces already present, though generally much weaker if their symmetry is lower. A transition is characterised by a small homogeneous distortion. However, as stated before, the magnetostriction, which may result from the magnetic ordering, may and also may not lead to a spontaneous distortion of the original crystal lattice.

The Jahn-Teller transitions involve changes in the character of the interatomic bonds. The Jahn-Teller effect, *Jahn, et al. [2]*, states that : when the electronic level of a molecule is degenerate at a structure of high symmetry, this structure is generally unstable and the molecule will have a structure of lower symmetry. Stability and orbital degeneracy are not possible simultaneously unless the molecule is a linear one, i.e. unless the atoms of the molecule lie on a straight line. In a simple structure, the onset of the effect may result in a displacive transition to a lower-symmetry hettotype, e.g. in $DyVO_4$ at 13.8 K.

A crystallographic phase transition results, in general, in two significant changes of a diffraction pattern :

(1) A shift or splitting of the reflections due to the changes of the unit cell. This requires accurate determination of the angular positions of the peaks (Bragg's angle $2\theta_B$). In such case, X-ray diffraction is well suited, while neutron diffraction with its poor angular resolution is not adequate.

(2) A change of the diffraction intensities due to shift in the atomic positions in the unit cell. Neutron diffraction is more adequate to such changes.

1.2. TYPES OF MAGNETIC STRUCTURES :

The types of the magnetic structures are classified according to the different arrangements of spin vectors of