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NEUTRON TEXTURE INVESTIGATIONS ON NATURAL MT. ISA CHALCOPYRITE ORE. PART I: PREFERRED ORIENTATION OF ONE AND THE SAME CHALCOPYRITE SAMPLE BEFORE AND AFTER EXPERIMENTAL DEFORMATION

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Natural chalcopyrite samples from Mt. Isa, Australia were axially shortened with a constant strain rate of $3 \cdot 10^{-5}$ sec^{-1}, at a constant confining pressure of 300 (400) MPa and at different temperatures. Neutron diffraction texture analyses were carried out before and after experimental deformation on one and the same sample. The preferred orientation of the experimentally undeformed samples consists of three main orientation components, which become weaker with deformation at temperatures up to 200°C. One or two new components develop with the c-axes perpendicular to the principal strain direction. At a deformation temperature of 300°C two very different new components develop, the original components are completely dissolved.

KEY WORDS: Chalcopyrite, experimental deformation, temperature, neutron diffraction, preferred orientation, pole figure

INTRODUCTION

The tetragonal structure of chalcopyrite ($CuFeS_2$) is a derivative of the cubic sphalerite structure (ZnS), where the Cu and Fe atoms alternately occupy the Zn positions along the c-direction. Thus, the unit cell is doubled in c-direction, the ratio a_o/c_o being 1.97. Identical reflections in the cubic system (e.g. (200) = (002)) are partially overlapping double reflections for chalcopyrite (e.g. (200/004)). In X-ray texture goniometry only incomplete pole figures of the pseudocubic (112) and (220/204) reflections can be measured. After axial shortening at 25°C (Lang, 1968) to 450°C (Jansen *et al.*, 1993) chalcopyrite shows a maximum of the (220/204) double reflection perpendicular to the principal strain direction. Lang interpreted the chalcopyrite preferred orientation as a (220/204) fiber texture similar to the (220) fiber texture of sphalerite (Siemes *et al.*, 1994).

Chalcopyrite deformation experiments at temperatures up to 500°C have been performed by Atkinson (1974), Kelly and Clark (1975) and Roscoe (1975), but without accompanying texture analysis.

A successful separation of the chalcopyrite double reflections was obtained by neutron diffraction. The measurements were carried out at the FRJ-2 reactor, KFA Jülich using a position sensitive detector (PSD) and a subsequent peak profile analysis (Jansen *et al.*, 1991, 1993). Five samples from Mt. Isa axially shortened at temperatures of 25, 100, 200, 300 and 400°C were investigated. The measured (112), (200), (004), (220), (204), (312), (116), (224), (400) and (008) pole figures were usable to evaluate the preferred orientation. The pole figures of the samples shortened at low temperatures showed four, at higher temperatures two main orientation components, but no fiber texture was detectable. The interpretation of this texture requires the knowledge of the texture of the undeformed material, but X-ray measured slices of the undeformed material didn't show a clear preferred orientation. Thus, a new testing series seemed to be necessary to study the bulk texture of the same sample before and after experimental deformation by neutron diffraction. As the FRJ-2 reactor in Jülich didn't operate during the last years the neutron measurements were performed at the FRG-1 at Geesthacht, GKSS-Research Centre. But, as the instrument wasn't equipped with a PSD at that time, another method to separate the chalcopyrite double reflections has to be used.

STARTING MATERIAL AND DEFORMATION EXPERIMENTS

Cylindrical specimens of 15 mm diameter and 30 mm length were prepared from the Mt. Isa chalcopyrite ore, which had already been used for earlier deformation experiments (Jansen and Siemes, 1993; Jansen *et al.*, 1993). The ore consists of 85% chalcopyrite, 3% pyrrhotite, 1% pyrite and 11% quartz and other minerals, the average grain diameter of chalcopyrite being 0.3 mm. Eight samples were axially shortened at a constant confining pressure of 300 MPa (400 MPa for room temperature) and with a constant strain rate of about $3 \cdot 10^{-5}$ sec^{-1}. Two experiments at temperature of 25, 100, and 200°C, and one experiment at 300 were performed, one experiment at 400°C failed after a few percent strain. Details of the experimental conditions are given in Table 1.

NEUTRON TEXTURE ANALYSIS

The texture measurements were performed at TEX-2, the neutron texture diffractometer

Table 1 Deformation experiments

Sample No.	*Temperature (°C)*	*Strain rate (sec^{-1})*	*Total strain (%)*	*Run dur.*	*$\Delta\sigma$ ($\varepsilon = 10\%$) (MPa)*
1 CH8311	25	$2.6 \cdot 10^{-5}$	16.14	2.0h	888
2 CH8307	25	$2.5 \cdot 10^{-5}$	17.26	2.1h	783
3 CH8318	100	$2.4 \cdot 10^{-5}$	9.54	1.4h	(807)
4 CH8310	100	$2.6 \cdot 10^{-5}$	17.34	2.1h	748
5 CH8302	200	$2.7 \cdot 10^{-5}$	18.28	2.1h	524
6 CH8219	200	$2.8 \cdot 10^{-5}$	20.45	2.2h	488
7 CH8320	300	$2.7 \cdot 10^{-5}$	19.56	2.1h	335

Table 2 Calculated positions and intensities of the important chalcopyrite reflections for a neutron beam of 0.134 nm wavelength using LAZY PULVERIX (Yvon *et al.*, 1977).

(hkl)	*2Theta*	*I (%)*
(101)	16.31	1.5
(112)	25.44	100.0
(200)	29.31	15.5
(004)	29.75	7.5
(220)	41.93	31.5
(204)	42.25	62.2

at GKSS Research Center (Brokmeier, 1989). The structural data of chalcopyrite were used to calculate the theoretical 2-Theta positions of the reflections for a wavelength of 0.134 nm (Cu(111) monochromator). Table 2 gives the first and strongest reflections of the spectrum. Only the weak (101) and the strong (112) reflections are measureable as single reflections. For testing purposes two different chalcopyrite sample cylinders were chosen, one experimentally undeformed and one experimentally shortened by 30% at 400°C (Jansen *et al.* 1993). Complete pole figures of the (101), (112) reflections and the (200/004), (220/204) double reflections were measured for both of the samples. The counting time for the (112) reflection was 2.5 hours, for the weaker reflections it was increased: 3.5 times for (200/004) and 7 times for (101). The (101) and (112) pole figures were also used to calculate orientation distribution functions (ODFs) by means of the iterative series expansion method using the positivity condition (Dahms and Bunge, 1989; Dahms, 1992). From the ODFs the (101) and (112) pole figures were recalculated, and showed a very good agreement with the measured ones. The ODFs were also used to calculate the (200), (004), (220) and (204) pole figures. The result of the pole figure calculation using only two sets of pole figures and only one with tetragonal information for the ODF calculation had to be verified. The calculated (200) and (004), as well as (220) and (204) pole figures were weighted with their theoretical intensities and added in order to obtain the superimposed sum pole figures (200 + 004) and (220 + 204). The sum pole figures were compared with the corresponding measured pole figures (200/004) and (220/204) of the overlapping reflections. Figure 1 shows that the agreement of the compared pole figures is very good for the undeformed sample CH8320 as well as for the deformed sample CH8410.

So the texture analysis procedure for all undeformed and afterwards deformed samples was the following: measuring the (101) and (112) pole figures, calculating the ODF, recalculating the (101) and (112) pole figures and calculating the (200), (004), (220) and (204) pole figures from the ODF.

PREFERRED ORIENTATION BEFORE EXPERIMENTAL DEFORMATION

Before using the neutron diffraction technique for texture analysis, slices from bottom and top of the undeformed sample cylinders were measured by X-ray diffraction. Examples of incomplete X-ray measured (112) and (220/204) pole figures in Figure 2 show, that it was not possible to identify a pervading preferred orientation for the

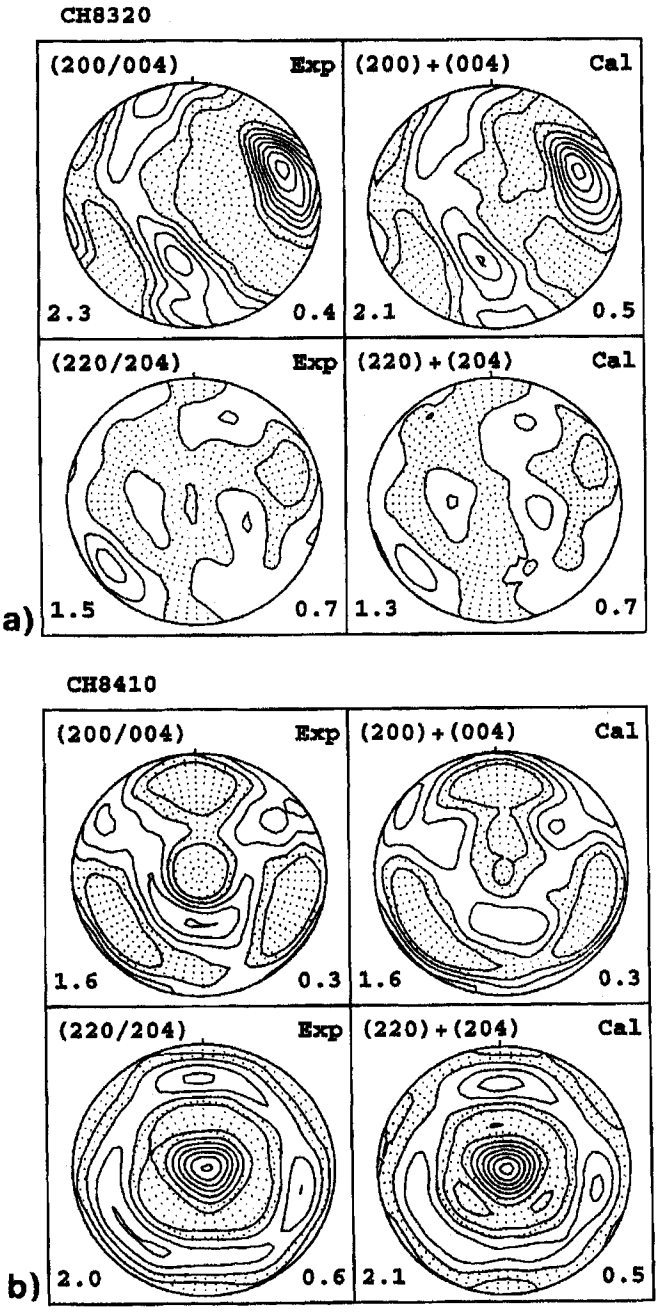
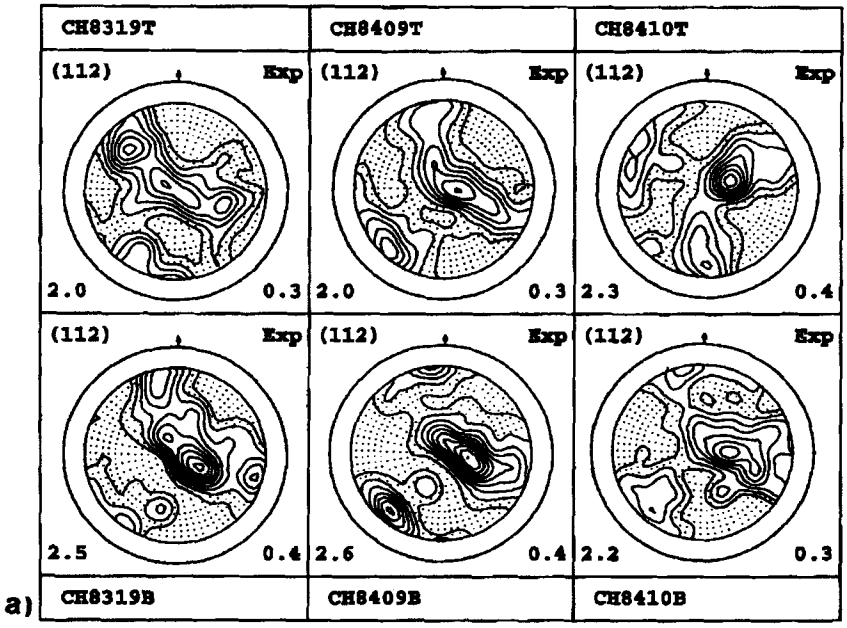


Figure 1 Neutron measured (200/004) and (220/204) pole figures compared to calculated (200) + (004) and (220) + (204) sum pole figures, a) sample CH8320 (undeformed), b) sample CH8410 (experimentally deformed); equal area projection, dotted areas: intensities below 1, contour interval: 0.2, bottom left: maximum, bottom right: minimum intensity.



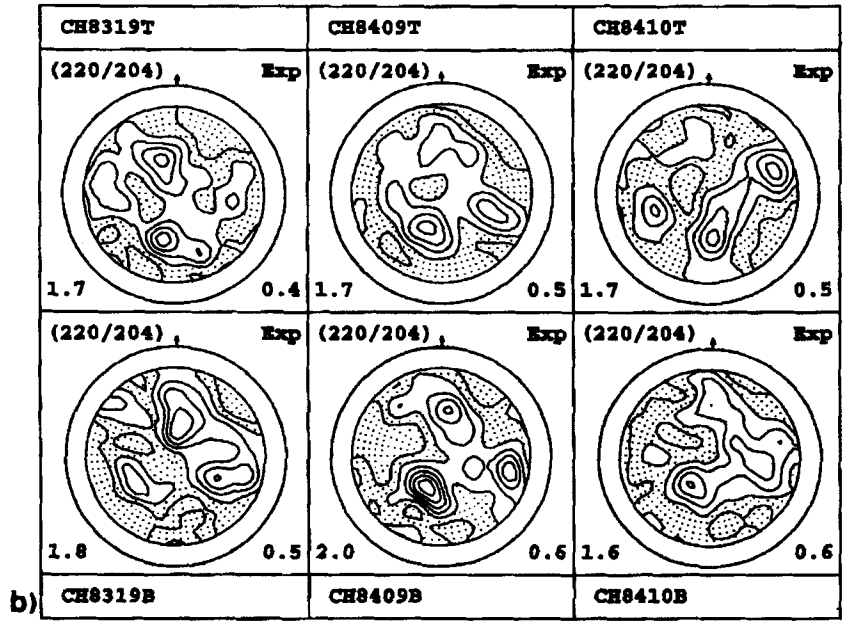


Figure 2 X-ray measured incomplete a) (112) and b) (220/204) pole figures from top (T) and bottom (B) slices of undeformed chalcopyrite sample cylinders; equal area projection, dotted areas: intensities below 1, contour interval: 0.2, bottom left: maximum, bottom right: minimum intensity.

Mt. Isa ore handspecimen. However, the neutron texture analysis gives evidence of a distinct preferred orientation of the ore. The neutron measured complete (101), (112) and calculated (004) pole figures of the eight investigated samples are given in Figure 3. Comparing the measured (101) and (112) pole figures (EXP) with the recalculated ones (REC) in Figures 4–7, a very good agreement is demonstrated. The (101) pole figures, although essential for the calculation, cannot give much visible information. The pseudocubic (112) pole figures show a quasi single crystal orientation, where the maxima are nearly spread to small circle distributions. More information is visible in the (004) pole figures, where similar maxima positions are marked with the same symbols 1, 2 and 3. The (004) pole figures of all samples show three main orientation components slightly different in position and intensity of the maxima, but very similar.

This is also proofed for the other pole figures by using the component fit program of Helming and Eschner (1990). Component 1 is the strongest for six of the eight samples.

PREFERRED ORIENTATION CHANGES AFTER DEFORMATION

After deformation at 25, 100 and 200°C (Figures 4–6a,b) the original three orientation components are still existing, but of weaker intensities and also slightly shifted their positions. From parts of the original components 3 and 1 two new components A and B have developed with the c-axes perpendicular to the principal strain direction. These components are responsible for the new central maximum of (220) for each of the six samples. For five of the six samples component A, near the samples' north direction, is stronger. Only sample CH8307 (Figure 4b) shows a more pronounced component B. Also central maxima of (101) and (204) are found after deformation at 25 and 100°C, which are produced by the relics of all three original orientation components. After deformation at 200°C the fraction of the original components is more reduced, there is no central (101) maximum detectable, but still a (204) maximum (Figure 6a, b). After deformation at 300°C the original components disappeared (Figure 7). Besides the new component A, which developed from the original component 3, another new component C developed, probably from component 1, 2 and 3, with (004) about 45 degrees off the center of the projection. In contrast to the other samples, this new component C produces the central (204) maximum for this sample, and a minimum in the center of (101). The pole figures of this sample at least give an intimation of a fiber texture. The differences in preferred orientation between a deformation temperature of 300°C and lower temperatures point to a change in deformation mechanisms.

CONCLUSIONS

For the special problem of the chalcopyrite preferred orientation the superiority of the neutron beam over the X-rays in texture analysis is evident. As the total specimen volume is measured by neutron diffraction, the statistics of the weak tetragonal (101) reflection of chalcopyrite is sufficient for the ODF calculation. And as the same specimen volume can be measured before and after experimental deformation, real differences in preferred orientation induced by the deformation processes are observable.

If the original texture of a material in axial shortening experiments is a random

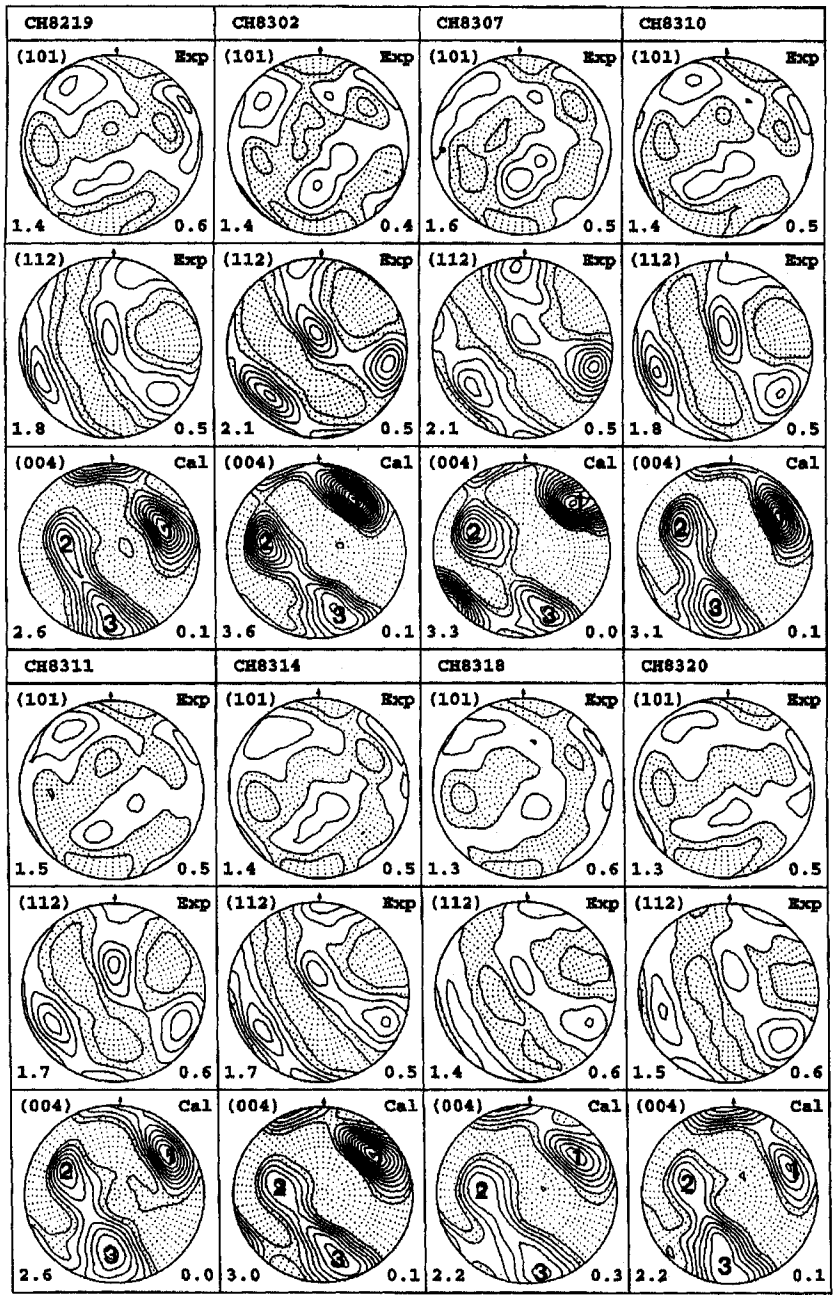


Figure 3 Neutron measured complete (101) and (112), and ODF calculated (004) pole figures of the 8 investigated chalcopyrite samples; equal area projection, dotted areas: intensities below 1, contour interval: 0.2, bottom left: maximum, bottom right: minimum intensity.

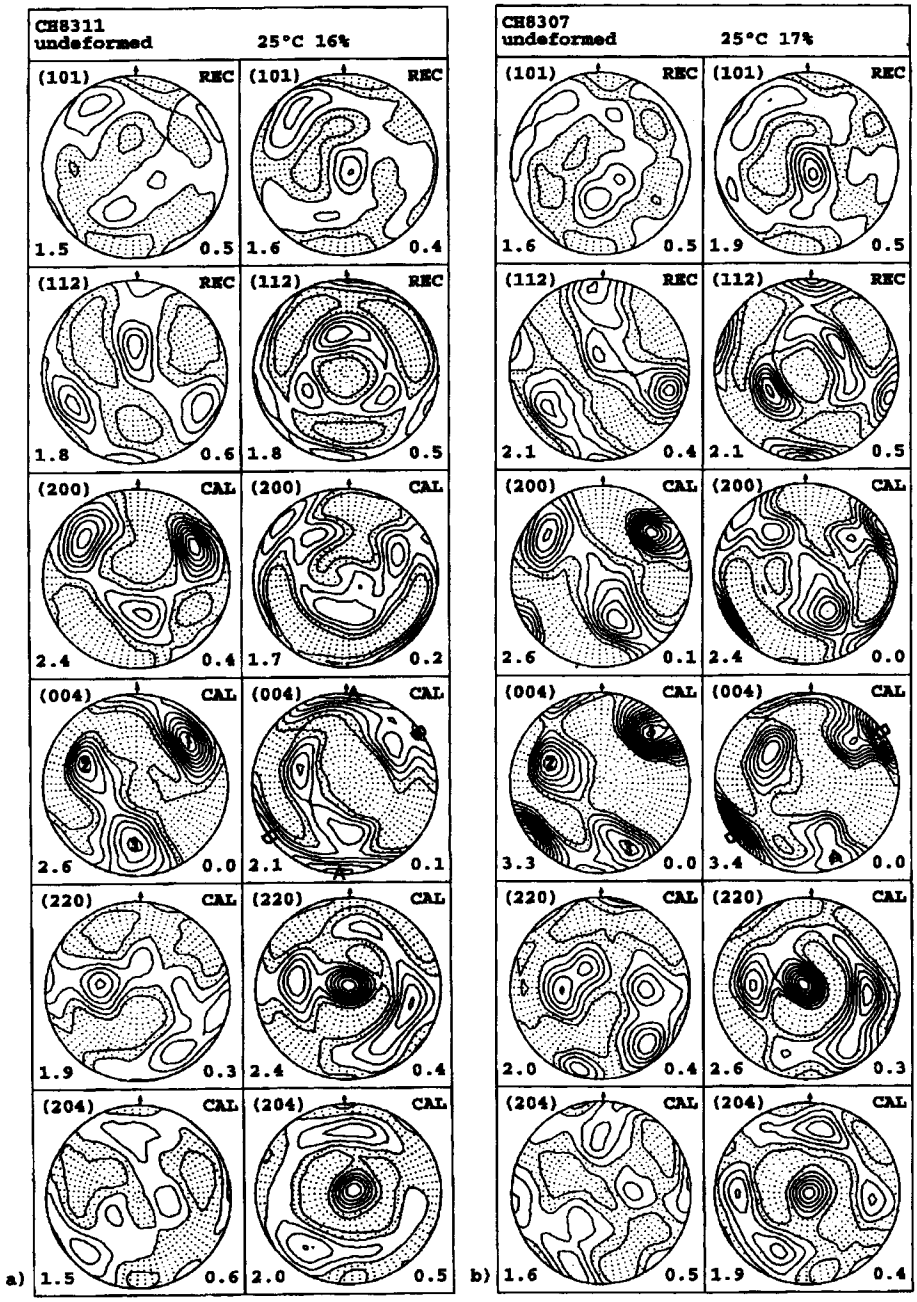


Figure 4 ODF recalculated complete (101) and (112), and calculated (200), (004), (220) and (204) pole figures of sample a) CH8311 and b) CH8307 before and after experimental deformation at 25°C; equal area projection, dotted areas: intensities below 1, contour interval: 0.2, bottom left: maximum, bottom right: minimum intensity.

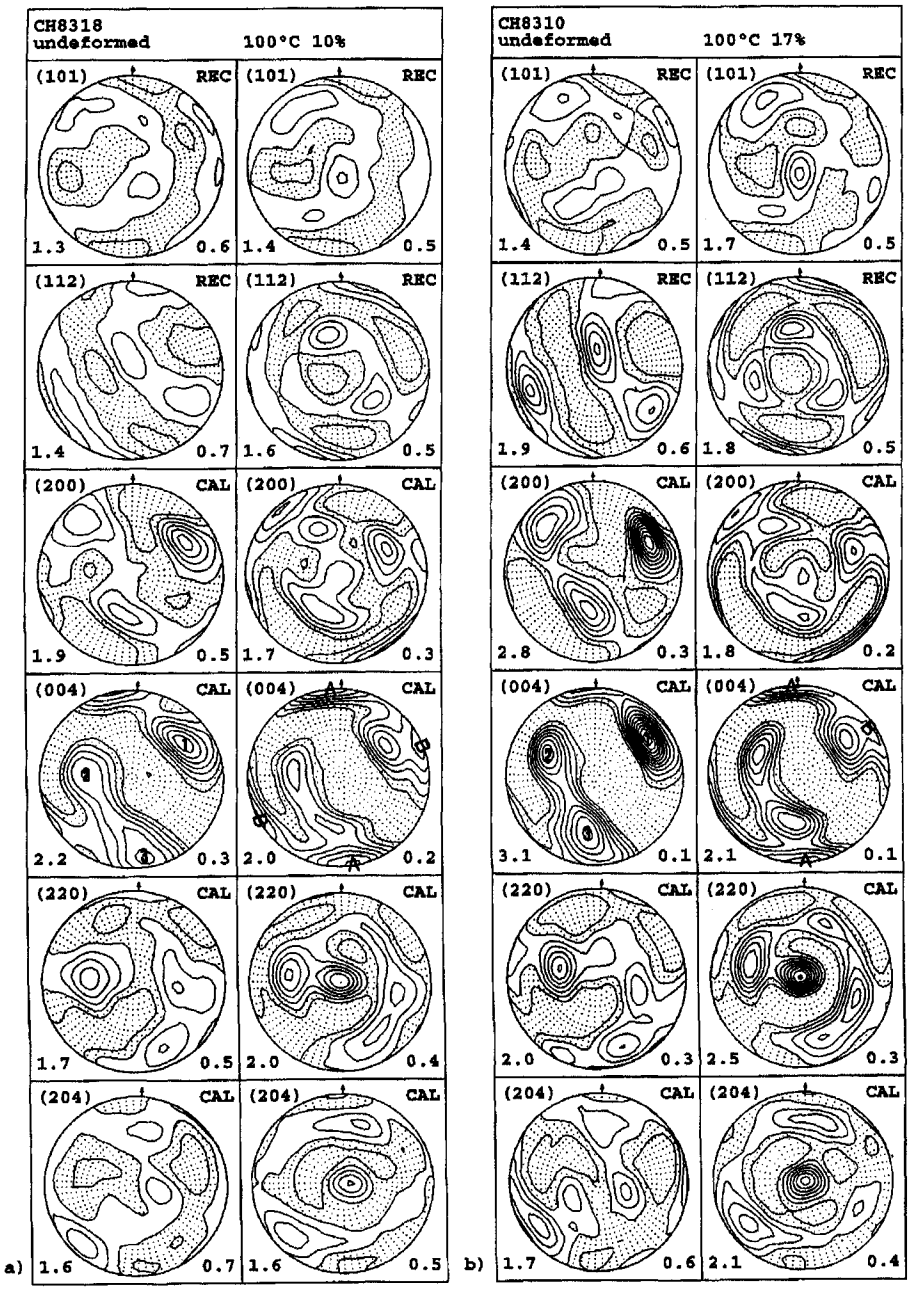


Figure 5 ODF recalculated complete (101) and (112), and calculated (200), (004), (220) and (204) pole figures of sample a) CH8318 and b) CH8310 before and after experimental deformation at 100°C; equal area projection, dotted areas: intensities below 1, contour interval: 0.2, bottom left: maximum, bottom right: minimum intensity.

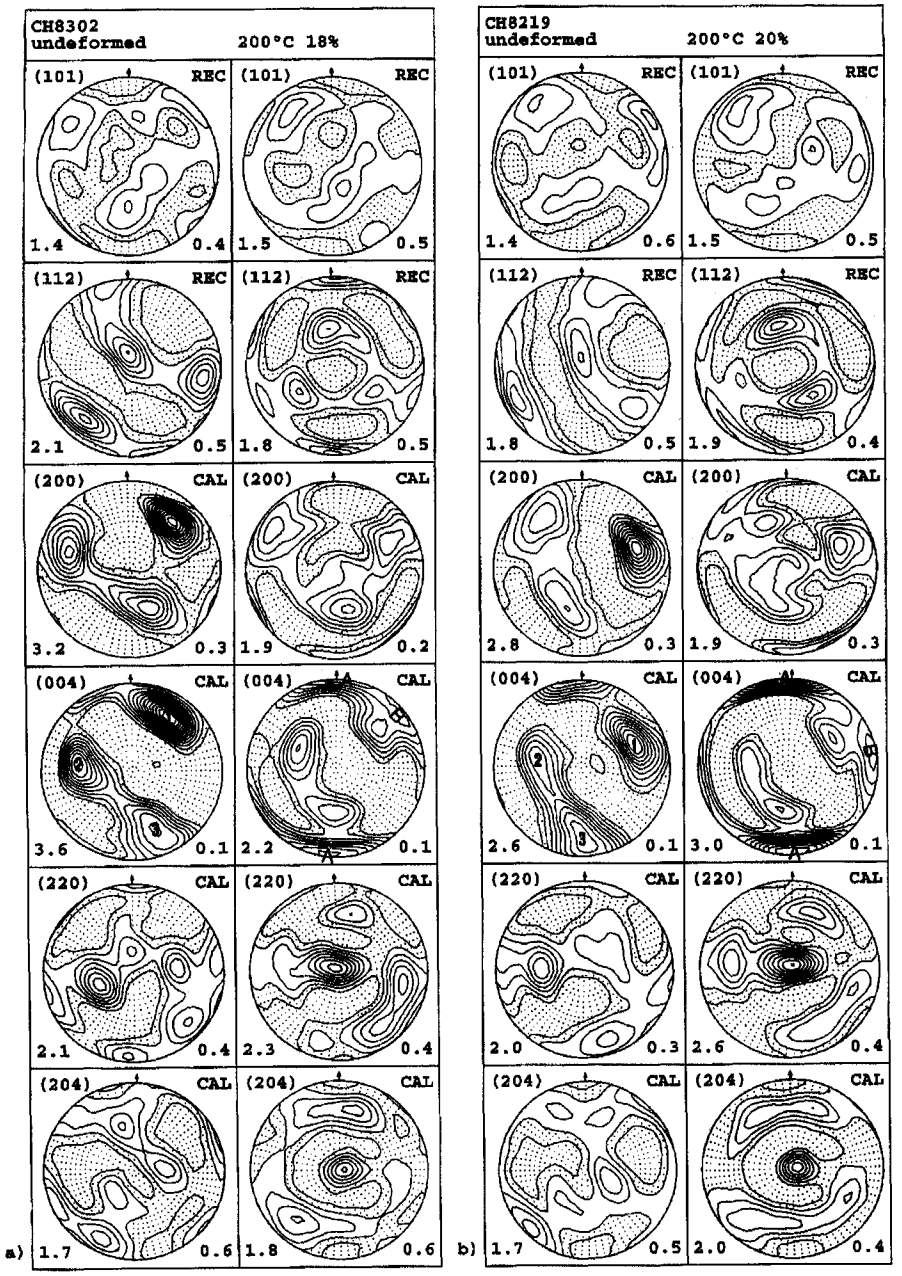


Figure 6 ODF recalculated complete (101) and (112), and calculated (200), (004), (220) and (204) pole figures of sample a) CH8302 and b) CH8219 before and after experimental deformation at 200°C; equal area projection, dotted areas: intensities below 1, contour interval: 0.2, bottom left: maximum intensity, bottom right: minimum intensity.

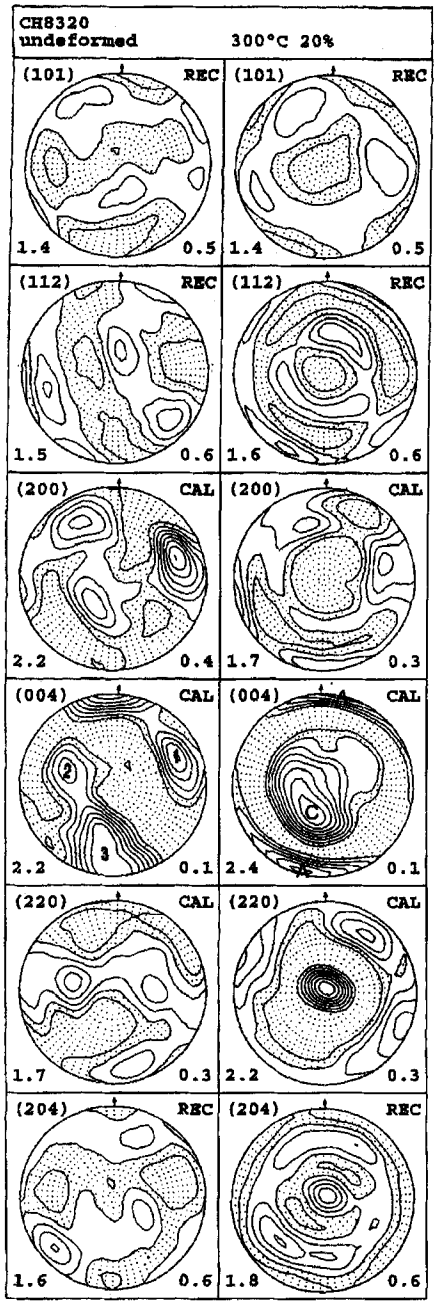


Figure 7 ODF recalculated complete (101) and (112), and calculated (200), (004), (220) and (204) pole figures of sample CH8320 before and after experimental deformation at 300°C; equal area projection, dotted areas: intensities below 1, contour interval: 0.2, bottom left: maximum intensity, bottom right: minimum intensity.

distribution, the development of an axial symmetric preferred orientation, a fiber texture, will start at once and will be visible after a few percent strain. A resulting fiber texture was not reached for the Mt. Isa chalcopyrite ore under the applied experimental conditions. In this case a detailed knowledge of the original preferred orientation, which is responsible for this effect, is of great importance. New orientation components can only develop from the original ones, and the deformation mechanisms strongly depend on the orientation of the crystallites to the strain direction.

The combination of four main orientation components, after low temperature deformation, and of two components, after high temperature deformation, of earlier neutron texture investigations on Mt. Isa chalcopyrite (Jansen *et al.*, 1993), can now be explained in the same way as the components in this study. Two different new components developed after deformation at high temperatures, and at lower temperatures one stronger new component besides the relics of the three original components are found.

A change in deformation mechanisms, which is reported for single crystals to occur between 200°C and 400°C (Hennig-Michaeli and Couderc, 1989), is confirmed in the present study to take place between 200°C and 300°C.

The results of the present study, particularly the knowledge of the original preferred orientation of the Mt. Isa material, lead to the conclusion, that further neutron diffraction texture analyses on the complete extensive series of earlier deformed Mt. Isa chalcopyrite samples (Jansen *et al.* 1993) can give more information about chalcopyrite deformation behaviour (Part II of this contribution, Jansen *et al.*, 1995).

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