16-Molecular Structure Determination by Methods other than Diffraction

The crystal structures of N-trichloroacetyl-glycine, TCA-G, N-trichloroacetyl-DL-alanine, TCA-DL-A, N-trichloroacetyl-L-alanine, TCA-L-A have been determined. The ^{35}Cl NQR, spectra of N-trichloracetyl amino acids and dichloroacetyl -glycine, -L-alanine, and -L-valine have been measured as function of temperature. Also the compounds of glycine, L-alanine with ClF_2CCOOH, of glycine, L-leucine with ClH_2CCOOH, of glycine and L-leucine with $Cl_2HCCOOH$ and of glycine and L-leucine with Cl_3CCOOH have been studied by ^{35}Cl NQR. The structures: TCA-G: $Pna2_1$, Z=8, (in pm and degree) a=1641, b=1002, c=1018; TCA-DL-A: C2/c, Z=8, a=3280, b=556, c=1031, β=96.68; TCA-L-A: P1, Z=2, a=967, b=949, c=619, α=74.97, β=74.20, γ=61.20.

The ^{35}Cl NQR frequencies have been observed in the range 41 ≥ ν/MHz ≥ 38, decreasing with increasing temperature. Part of the resonances bleach out at T_b, far below room temperature, leading to informations about the crystal structures at 77K. No phase transitions were observed by DTA between 77 and 295K.

The crystal structures will be discussed in connection with the spectroscopic results and conclusions will be drawn about the structures of the compounds for which ^{35}Cl NQR only is available..

PS-16.01.10 CRYSTAL STRUCTURE REFINEMENT AND SINGLE CRYSTAL ^{81}BR ZEEMAN NQR STUDY OF $KHGBR_3 \cdot H_2O$. By Hiromitsu Terao[a], Tsutomu Okuda[b], Sachiyo Uyama, Hisao Negita[a], Shi-qi Dou[c], and Alarich Weiss[c]. [a] Faculty of Integrated Arts and Sciences, Tokushima University, Minamijosanjima-cho, Tokushima 770, Japan. [b] Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashihiroshima 724, Japan. [c] Computer Center, Hiroshima University of Economics, Asaminami-ku, Hiroshima, Japan. [c] Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstr.20, D-6100 Darmstadt, Germany.

From ^{81}Br NQR Zeeman spectroscopy the electric field gradient tensors, EFGT, at the Br sites of $KHgBr_3 \cdot H_2O$ were determined in magnitude and direction of Φ_{xx}, Φ_{yy}, and Φ_{zz}. For Br(1) and Br(2) the bond directions r(Hg-Br) found in the structure determination [1] do not agree with the direction of Φ_{zz} we measured. Also for the bridging bromine Br(3) there is a discrepancy with the NQR results. Structure and ^{81}Br NQR are in contradiction. Therefore the crystal structure was redetermined. We find the same space group, $Cmc2_1$, Z = 4, a = 436.5(2)pm, b = 1689.6(5)pm, c = 1015.0(4)pm, nearly the same lattice constants as [1]. However the structure found differs from [1] in the atomic positions and the coordination model changes drastically. With the redetermination, ^{81}Br NQR and structure are in good agreement. The results of both methods will be compared and the chemical bond in the title compund will be discussed on the basis of an MO model.

[1]: V.M.Padmanabhan, V.S.Yadava, Acta Cryst. B25,647(1969)

PS-16.01.11 A STUDY OF FERROELASTIC DOMAIN STRUCTURE WITH INCOMMENSURATE/COMMENSURATE TWIN BOUNDARIES BY MEANS OF AFM, STM, ESR, ESR-CT AND X-RAY DIFFRACTION. By T. Kobayashi* and I. Takei, School of Pharmacy, Hokuriku University, Kanazawa, Japan and K. Yamana and S. Nakamura, Industrial Research Institute of Ishikawa, Kanazawa, Japan and M. Machida, Department of Physics, Faculty of Science, Kyushu University, Fukuoka, Japan.

The ferroelasticity of MP_5O_{14}(M:La-Tb) with commensurate domain boundaries and $LaNbO_4$ with incommensurate/W' ones (Sapriel, J., Phys. Rev., 1975, B12, 5128-) has been studied by DSC, polarizing microscope, X-ray diffraction, (Kobayashi, T. et al., J. Phys. Soc. Jpn., 1976, 40, 595-596), neutron diffraction (Horiuchi, H. et al., Jpn. J. Appl. Phys., 1991, 30, 2035-2039), ESR, ESR-CT, STM, and AFM. The domain structure near the boundary of GdP_5O_{14} observed by AFM (nanoscope II) is shown in Fig.1. The large noises (obstacles) on the surface are removed by using the least squares method for the AFM scanning line as shown in Fig. 2. The XY projection of domain boundary AB on the crystal surface is shown in Fig. 3, the YZ projection in Fig. 4. The ferroelastic domain front seems to be a zigzag configuration in the microscopic observation. The domain wall width can be estimated from our AFM data. The temperature dependence of ferroelastic domain boundaries of EuP_5O_{14} observed by STM is shown in Fig. 5. We observed the temperature dependence of monoclinic β angles, obtained by STM and X-ray diffraction(ω scan technique). According to Sapriel, $LaNbO_4$ should have incommensurate twin boundaries. The incommensurate twin boundaries, however, cannot be detected through our close analyses of neutron and X-ray diffractions by using the transformation matrix calculated from the UB matrix. Therefore if the incommensurate twin boundaries are supposed to exist, it is only close to the twin boundary wall. Our computer system of ESR crystallography will be also shown with the instruments(e.g. ESR 2/3-circle goniometer,ESR-CT etc.)developed specially for our experiments.

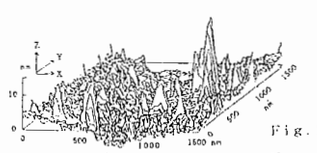

Fig.1

Fig.2

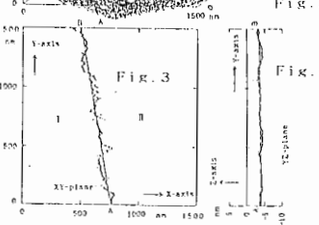

Fig.3

Fig.4

Fig.1 - Fig.4 Atomic force microscope (AFM) GdP_5O_{14}

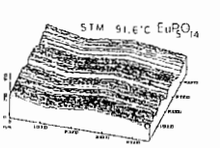

Fig.5a

Fig.5a - Fig.5b Scanning tunneling microscope (STM) EuP_5O_{14}

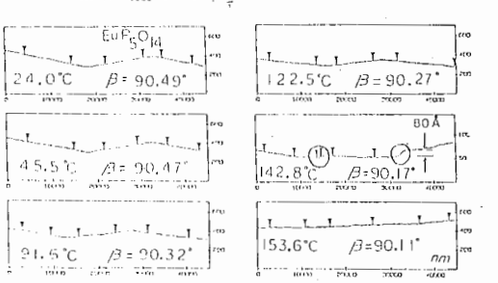

Fig.5b

