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PS-12.01.20 STRUCTURE OF THE INCOMMENSURATE PHASE OF 4,4′-DICHLORODIPHENYL SULPHONE AT 90 K. *By F. J. Zúñiga, J. M. Pérez-Mato* and T. Breczewski. Departamento de Fisica de la Materia Condensada, Facultad de Ciencias, Universidad del Pais Vasco, Apdo. 644, Bilbao, Spain*

The structure of the incommensurate phase of 4,4′-dichlorobyphenyl sulfone[1,2], $C_{12}H_8Cl_2O_2S$, has been determined at 90 K using the superspace formalism. The refinement of the atomic modulation of displacive type, wavevector $\mathbf{q}=0.780(2)\mathbf{b}^*$, has been performed in the superspace group P(I2/a):(s,-1), using main and first order satellite reflections. A model of the distortion including zero, first and second order harmonics has been considered in the modulation. The final agreement factors are R = 0.042, R_o=0.039 and R_I=0.043 for all, main and satellite reflections respectively. Second order harmonics are critical in the refinement as they decrease the R_I factor from 0.12 down to 0.043. The primary distortion is described by a mode of Λ_2 symmetry involving intermolecular motions and an important intramolecular twist of the phenyl groups. Crystal data of the average structure : T=90K, M_r=287.2, orthorhombic, I2/a, a=20.20(2), b=4.910(2), c=12.054(9)Å, β=90.02(4)°, V=1195(2) Å^3, Z=4, D_x=1.597 Mgm^{-3}, λ(Mokα)=0.7107 Å, μ=0.67 mm^{-1}, F(000)=584.

References

1- Pusiol, D. J., Wolfenson, A. E. and Brunetti, A. H. (1989). Phys. Rev. B40, 2523.
2- Kasano, H., Koshiba, T., Kasatani, H. and Terauchi, H. (1990). J. Phys. Soc. Jpn. Lett. 59, No. 2, 408.

PS-12.01.21 CHANGE OF STRUCTURE OF Co-ÅKERMANITE AT ELEVATED TEMPERATURES. By K. Hagiya, N. Haga, M. Ohmasa*, K. Ohsumi[1] and K. Iishi[2]
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Hemingway *et al.* (Canadian Mineral., 1986, 24, 425-434) and Seifert *et al.* (Phys. Chem. Minerals, 1987, 14, 26-35) found that each Bragg reflection in X-ray and electron diffraction patterns of synthetic åkermanite ($Ca_2MgSi_2O_7$) taken at room temperature is accompanied by a set of satellite reflections. These satellites indicate that the modulation in the material is incommensurate. They also reported that the satellite reflections decrease in intensity at elevated temperature and disappear at higher temperature. Similar phenomena were also found in electron diffraction patterns of synthetic Co-åkermanite, $Ca_2CoSi_2O_7$ (Iishi *et al.*, N. Jb. Miner. Mh., 1989, 1989, 219-226). The incommensurate modulation in the cobalt analogue was determined by five-dimensional refinement of the structure (Hagiya *et al.*, Acta Cryst., 1993, B49, in press). The results revealed that the modulation is caused by the shifts of the constituent atoms.

Temperature dependence of intensities of the satellites was examined *in situ* to determine the transition temperature between the incommensurate and normal phases and also to observe change of modulation of the structure. Synchrotron radiation was employed as an X-ray source, because the intensities of the satellites are weak and diminishment of them must be detected. A fragment of the sample was mounted in a small gas blow system with an electric heater attached on the Weissenberg camera at BL-4B in the Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Japan, and diffraction patterns were recorded on the imaging plate (Fuji Co.Ltd., Miyahara et al., Nucl. Instrum. Methods, 1986, A246, 572-578) at selected temperatures. The radius of the cylindrical camera is 100mm. The incident X-ray was monochromatized by 111 of Si crystal and the wave length 1.029Å was determined by calibration with diffraction of a GaP crystal. The temperature of the sample was varied from room temperature to 300°C at arbitrary intervals and was estimated from that measured by a thermocouple to regulate the furnace with a calibration curve determined before the experiments.

The observation of the satellites by synchrotron radiation revealed that their intensity decreases linearly from room temperature to 200°C and weakens to background level at about 216°C. Thus the transition temperature between the incommensurate phase to normal one was determined to be 216°C. The transition was ascertained to be reversible. The intensity of the satellites decreases linearly from room temperature according as the temperature raises, and becomes half at about 150°C. The reduction of the intensity is ascribed to the decrease of the amplitude of the modulation wave.

PS-12.01.22 CRYSTAL STRUCTURE OF NANOPARTICLES OF ZnS Binny Thomas and M Abdulkhadar*, School of Pure & Applied Physics, Mahatma Gandhi University, Ettumanoor, Kerala - 686 631 INDIA

Finding the crystal structure of nanoparticles, microcrystals or microclusters is a crucial and challenging problem in the study of their properties. The physical properties of microclusters have been reported to be critically dependent on their size and crystal structure. It is important to understand how the structural properties change as atoms, molecules and even small clusters of these come together to form progressively larger clusters and finally acquire the bulk structure. In microclustures, the surface atoms represent a large fraction of the volume of the material and the resultant excess free energy is expected to cause a contraction of the lattice without drastic changes in the crystal structure. The problem of determination of vital characteristics of small particles such as the morphology, structure and the lattice parameters becomes increasingly difficult as the size of the particles becomes smaller.The crystal structure and lattice parameters of these systems of particles is often ambiguous since the lattice will be generally disordered and the crystal structure will be anomalous.

Changes of lattice parameter of small metal particles with respect to the bulk values have been reported in many cases. The study of small particles of semiconductor materials are considered important since the electronic properties of small clusters of these materials may be different from the bulk electronic properties. Small particles of semiconductor materials such as CdS have been extensively studied by many researchers and it has been reported that for particles of size between 15 to 40 A , a unique structure does not exist. The authors report here the crystal structure of

