

05.2-20 CRYSTAL STRUCTURE OF ALKYLTHIO-SUBSTITUTED TETRATHIAFULVALENE AS A "MOLECULAR FASTENER" By Y. Higuchi, N. Yasuoka Himeji Institute of Technology, G. Saito Institute of Solid State physics, The University of Tokyo, and H. Inokuchi Institute for Molecular Science

Crystal structures of alkylthiosubstituted tetrathiafulvalene (TTC_nTTF: n=2,5,10) have been determined. Crystal data of each compound are, TTC2TTF P2₁/c, a=12.220(2), b=8.759(2), c=22.950(4) Å, β=96.69(2)°. TTC5TTF: P $\bar{1}$, a=9.031(3), b=17.604(3), c=5.367(1) Å, α=90.26(2) β=105.90(4), γ=90.85(2)°, TTC10TTF: P $\bar{1}$, a=7.850(3), b=32.960(9), c=5.115(4) Å, α=92.46(2) β=101.16(3), γ=88.18(3)°. The spatial arrangement of eight sulfur atoms in TTC2TTF was solved by the use of RANTAN program, whereas those in TTC5TTF and TTC10TTF are found in Patterson map. Remaining carbon atoms were revealed in a difference Fourier map. Block-diagonal least-squares refinement converged crystallographic R factors to 0.063(TTC2TTF), 0.058(TTC5TTF) and 0.055(TTC10TTF), respectively. For TTC5TTF and TTC10TTF, hydrogen atoms of alkyl chain could be found on difference Fourier map, and were included in the refinement.

The bond lengths and angles found in these compounds are in agreement with those in BEDT-TTF and TTC1TTF molecules. The central tetrathiotetrathiafulvalene moiety (C₆S₈) is almost planar for TTC5TTF and TTC10TTF, whereas some deviations from the planarity are recognized in TTC2TTF. In TTC5TTF and TTC10TTF, C₆S₈ moiety tends to stack uniformly along the shortest crystal axis (c-axis), and the molecular column is built up. For TTC10TTF, the shortest intermolecular S-S distance between adjacent molecules in the column is found to be 3.57 Å, which is remarkably shorter than the sum of the van der Waals radii (3.70 Å). The corresponding value for TTC5TTF is 3.73 Å. On the contrary, TTC2TTF molecules exhibit no tendency to form such uniform stacks. There are two kinds of intermolecular S-S distances along the direction of the stacking, namely 3.70 Å and 3.80 Å. These findings suggest the following. As the number of carbon atoms of the alkyl chain increases in this series of compounds, the molecules tend to build up uniform stackings and the intermolecular S-S distances between adjacent molecules decrease. This fact is considered to be attributed to the strong inter-alkylchain interactions between the adjacent molecules in the column. In other words, central C₆S₈ moieties of TTC5TTF and TTC10TTF have been found to be fastened by four long alkyl chains, whereas such an effect was not recognized in TTC2TTF structure. These findings from the crystal structure analyses are consistent with the results of the measurement of the electrical resistivity.

05.2-21 THE LOCAL TRIANGULAR ARRANGEMENTS OF Mn ATOMS IN REENTRANT-SPIN-GLASS OF Au-15 at.% Mn ALLOY. By K. Ohshima, Institute of Applied Physics, University of Tsukuba, Ibaraki 305, Japan and J. Harada, Department of Applied Physics, Nagoya University, Nagoya 464, Japan

In order to elucidate the relationship between the local arrangement of Mn atoms and the peculiar magnetic property, i.e., reentrant-spin-glass behaviour for Au-15 at.% Mn alloy, atomic short-range order (ASRO) parameters were determined from an analysis of X-ray diffuse scattering intensities measured at room temperature. Local structure of Mn atoms was simulated with the use of computer, on the basis of the ASRO parameters obtained. The Mn atoms in the ASRO state form a three dimensional irregular network which is linked by linear chain segments along the [100] directions and also with nearest-neighbour relations. This is a similar structure to the case of Au-20 at.% Mn alloy but somewhat more irregular than that (Suzuki et al., Acta Cryst., A38 (1982) 522-529). Assuming that the first-nearest Mn-Mn pairs have antiferromagnetic coupling, while those at the second neighbour distance are ferromagnetically coupled, a spin configuration was assigned to this irregular Mn network based on the Ising spin system: several types of ferromagnetic clusters were found to exist, and they are connected with one another by antiferromagnetic coupling. It is occasionally found that there are triangular arrangements of Mn atoms linked with nearest-neighbour relations, whose spin configuration can not be assigned uniquely. Since such triangular arrangements of Mn atoms are not isolated but are a part of the three dimensional irregular network, it is possible to say that many spin configurations corresponding to the ground state exist in the ASRO state of this alloy. This ASRO arrangement of Mn atoms seems to play an important role for the reentrant-spin-glass behaviour. Fig. 1 shows an example of three possible spin configurations around a double triangular arrangements of Mn atoms where the Ising spin system is also assumed. Solid and open circles represent different spin orientations.

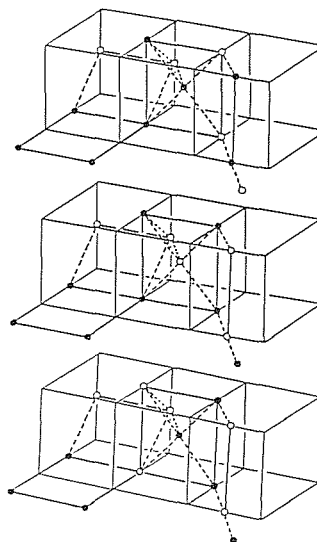


Fig. 1