Ramaseshan and anomalous scattering*

Writing this short note gives me an excuse for a little reminiscence and a wonderful opportunity to recount my years with S. Ramaseshan (SR) in the Physics Department, Indian Institute of Science, Bangalore. Interestingly it turns out that 50 years have passed since I joined him in August 1953!

R. S. Krishnan (1911–1999), the then Head of the Department of Physics, took me to SR in the X-ray laboratory and told him that I would be his student. SR was a tall, handsome and good looking young man with a ready smile. He talked with me in a friendly manner—gentle and warm. What he said at the end of the conversation gave me a tremendous shock when he mentioned that he himself was new to the subject of X-ray crystal structure analysis and we would learn it together! In all innocence I hastened to ask whether it would be a good idea to start determining an already well worked out crystal structure of a simple compound. That he did not throw me out of his room is, in retrospect, a great surprise to me, revealing his great tolerance and sympathy towards an uninformed student. Before long, I realized how extremely fortunate I was to have joined him as his first student in the field of X-ray crystallography. He was thinking deeply about the phase-problem and an experimental way of solving it. He told me about the anomalous scattering of X-rays and discussed the feasibility of determining the phases of Bragg reflections in the case of centrosymmetric crystals.

S. Ramaseshan speaking as Vice-President of the International Union of Crystallography at the Hamburg Congress in 1984.

*Dedicated to Prof. S. Ramaseshan on his 80th birthday.

When the frequency of the incident X-ray radiation is such that it is strongly absorbed by one or more elements in a non-centrosymmetric crystal Friedel's law $[(I(hkl) = (I(\bar{h}\bar{k}\bar{l})]$ breaks-down. Bijvoet *et al*. from Utrecht were the first to demonstrate that the anomalous scattering could be used to determine the absolute configuration of a chiral molecule[1]. They established the absolute stereochemistry of the anion in the crystalline double salt of rubidium sodium (+) – tartarate. Making use of the break-down of Friedel's Law, Bijvoet with his coworkers[2] and independently G. N. Ramachandran and S. Raman[3] showed that the phase angles were calculable. They determined the crystal structures of two different optically active molecules. On the other hand, SR concentrated his attention on the solution of centrosymmetric crystals via anomalous scattering.

However, in the case of a centrosymmetric crystal Friedel's law does not fail as in the case of a non-centrosymmetric crystal. So a different approach had to be thought of. It was well-known that the phase problem could be solved by the isomorphous replacement technique. The method is based on using the intensity data of isomorphous crystals and from knowledge of the position of the replaceable atoms, which have different scattering power for X-rays. It follows immediately that the use of two appropriate wavelengths close to the absorption edge of one of the atoms in the crystal would in effect be equivalent to the substitution of one of the atoms in the crystal by another of a slightly different scattering power. N. V. Mani and I were involved in this investigation which excited us a great deal. The substance chosen for the study was potassium permanganate ($KMnO_4$). Multiple-film Weissenberg photographic method was used for the data collection with CuKα, CoKα and FeKα radiations, all of which were close to the K-absorption edge of the Mn atom. The changes induced in the scattering power of Mn atom for these wavelengths being small, the difference in the intensity of the X-ray reflections was not expected to be large. This meant that extremely careful measurements were needed to obtain a reliable set of intensity data sets. We were most delighted that the crystal structure could be solved using this method in a straightforward manner[4]. It may be mentioned that the method has not been utilized any longer mainly owing to the outstanding success of the direct methods for determining the phases of X-ray reflections.

Soon after the successful completion of the study described above, SR proposed a novel approach for solving the phase problem in non-centrosymmetric crystals. In a nutshell, the method requires collecting data by using two incident wavelengths on each side, close to the absorption edge of one of the atoms. Since for one of the wavelengths there is only an amplitude change ($f' \neq 0$ but $f'' = 0$ in the expression $f = f_0 + f' + if''$) and for the other there exist changes both in phase and amplitude ($f'' \neq 0$), the method could, in principle, be used for the unequivocal determination of the phases of non-centrosymmetric crystals[5].

The idea of using the anomalous neutron scattering for phase angle determination was described by SR at the Annual Meeting of the Indian Academy of Sciences in 1965 (ref. 6). The values

S. Ramaseshan presents G. N. Ramachandran the Festschrift brought out in honour of the latter in 1992.

of anomalous dispersion effects b' and b'' (the scattering length $b = b_o + b' + ib''$) are much greater than f' and f'' for X-ray scattering. For example, for ^{113}Cd, $b'' \sim 10\, b_o$ and $b' \sim 5\, b_o$ on the shorter wavelength side. SR showed that if the crystal contains a ^{113}Cd atom per asymmetric unit and if it scatters anomalously, a structure containing as many as 10,000 atoms could be determined via the anomalous neutron scattering method. With ^{147}Sm or ^{157}Gd in the crystal, the number of light atoms could increase three or four fold. Thus the method should, in principle, allow the determination of the structures with a very large number of light atoms. Unfortunately, the practical application of the method is beset with experimental problems, mainly arising from the nonavailability of very powerful neutron radiation sources.

The research group led by SR during the period 1953–1960 consisted of six research scholars—M. A. Viswamitra N. V. Mani, S. Swaminathan, H. Manohar, Jelica Musovic (from Yugoslavia) and myself. Investigations on different aspects of X-ray crystallography—the anomalous dispersion technique, organic and inorganic crystal structures and high temperature crystallography were undertaken. He provided the right kind of intellectual environment by encouraging a lot of informal discussions on each other's crystallographic problems. The simplicity and directness of his physical intuition were striking; gifts which one can experience even now at the age of 80 when he is not in the best of health.

Let me go back to the beginning of this note where I expressed my shock during my first encounter with SR. How stupid I was became obvious to me very soon and indeed I began to wonder as my scientific training progressed, 'how such a small head could carry all he knows'. I am very fortunate to be associated with such a brilliant scientist and a wonderful human being for five decades. I wish him good health on his 80th birthday.

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