CHARGE and SPIN DENSITY

By R. J. Weiss

SPECIFICATIONS—US ARMY TANK—JULY 2064 . . . medium tank, 4 passenger, armour plated steel, maximum speed 120 mph . . . .

Wave functions must be specified to within 1% at all points in the atomic polyhedra. One electron observables to be evaluated . . . .

The above excerpt might be taken from specifications for an Army tank in the year 2064 since high-speed computers may then be capable of calculating all pertinent observables (strength, hardness, thermal conductivity, etc.) from the wave functions. However, projected military requirements a hundred years hence had little to do with the Army's sponsorship of the Sagamore conference on charge and spin density (Aug. 17-21, 1964), which resulted rather from an active interest of the research group of the US Army Materials Research Agency at Watertown, Mass., in the measurement and calculation of charge and spin density.

The conference at the former Vanderbilt Estate at Sagamore (Racquette Lake, N. Y.) was the first international conference devoted exclusively to the measurement and calculation of charge and spin density on atoms (both free atoms and in solids). The conference center at Sagamore is most efficiently administered by Syracuse University. It is an ideal location due to its privacy, generally good summer weather, numerous recreational facilities and comfortable accommodations. Approximately sixty people representing Japan, France, United Kingdom, Italy, Germany, Portugal, Australia, Norway, Holland, Israel and the USA attended. The meeting consisted of six sessions each commencing with a review paper and followed by informal contributions and discussions.

With very careful work absolute structure factors can be measured with x rays to an accuracy of about one percent. However, such accuracy has only been achieved in a very limited number of cases, such as the inert gases, Ne, Ar, Kr, and Xe, and the solids, Al, Fe, Cr, Cu, diamond, Si, and Ge. The problems encountered in converting the measured structure factors into a charge density have not been adequately solved since the data can only be taken over a limited range of $\sin\theta/\lambda$. Hence, one generally attempts to compare his measured structure factors with calculated ones. In the case of the inert gases, good agreement is obtained with Hartree-Fock free-atom scattering factors, but large differences (4-5 percent) exist between the observed scattering factors of the metals Al, Cr, Fe, and Cu and the Hartree-Fock free-atom values. These differences may result from bonding effects in Cr, Fe, and Cu, but the effect appears too big in Al, and there it requires an appreciable expansion of the core electrons ($1s^2$, $2s^2$, $2p^6$). Good agreement with the Hartree-Fock free-atom radial wave functions is obtained in the semiconductors diamond, silicon, and germanium, with the added observation that the angular part of the charge density in Si and diamond points toward the tetrahedrally coordinated nearest neighbors. This observation comes principally from the "forbidden" (222) reflection.

Hartree-Fock wave functions are believed to provide x-ray scattering factors to an accuracy of one percent, but these are only available for free atoms. In the case of simple molecules, Roothaan has obtained accuracies in the charge density approaching that of the Hartree-Fock method. Calculations for solids are appreciably less accurate. A strong recommendation was made for theoreticians, particularly those interested in energy bands, to calculate the x-ray scattering factors. To date, such efforts have been primarily limited to the case of diamond with limited success.

Absolute magnetic scattering factors can be measured to better than one percent with neutrons, particularly when one is able to use

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polarized neutrons. A large number of elements, compounds, and alloys have been studied, e.g., Fe, Ni, Co ferromagnetic Pt and Pd alloys, NiO, MnF_2, several rare earths, and paramagnetic Va, the last by application of an external magnetic field. While the general shape of the form factor curves corroborates the $3d$ like character of the spin density in the first group of transition elements, appreciable differences exist between calculated free-atom values and the observed values in solids. Considerable effort has been expended to understand these differences through crystalline effects but with limited success. In the case of antiferromagnetic MnF_2, Nathans and coworkers have been able to show the distribution of spin density on the fluorine atoms, which is a manifestation of the super-exchange process. In Fe, Ni, Co, and NiO, one finds clear indications of the $3d$ electron distribution in a cubic crystalline field with the spin density favoring the doubly degenerate (e_g) orbitals in Fe, Co, and NiO and the triply degenerate (t_g) orbitals in Ni.

Differences in the angular distribution of polarized positron annihilation in ferromagnets have been observed by reversing the magnetization relative to the polarization direction but no clear interpretation of these differences is forthcoming.

Entertainment was provided by the Krasner string quartet and by the after-dinner talk of Professor R. Brill of Berlin. Professor Brill is director of the Fritz-Haber-Institut in Berlin. He is well known for his pioneer work on charge-density measurements particularly in diamond. Following the war Professor Brill came to the US Army Signal Corps Laboratories at Fort Monmouth under the so called "operation paperclip". After some ten years at Brooklyn Polytechnic Institute Professor Brill returned to his present post in Germany.

While the bulk of the participants were primarily concerned with x-ray and neutron diffraction there was a limited amount of interest in NMR and Mössbauer measurements of charge density at the nucleus. In order to keep the number of participants under one hundred the program committee did not emphasize such work. The program committee consisted of B. Batterman, A. J. Freeman, R. Nathans, C. G. Shull, R. J. Weiss, and V. Weiss, secretary.

It is intended to establish a roster of those *actively engaged* in the measurement and calculation of charge and spin density. Those wishing to be placed on this roster are asked to write to R. J. Weiss, US Army Materials Research Agency, Watertown, Mass.