X-Ray, Electron, and Neutron Diffraction

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THE CONTRIBUTIONS WHICH HAVE BEEN made to our knowledge of atomic, molecular, and crystalline structure by studies involving X-ray diffraction constitute a well-known chapter in the progress of physics. This is to some extent also true of the newer field of electron diffraction. The new field of neutron diffraction, which has been made possible by chain-reacting piles, promises to be a useful partner to the above fields in molecular and crystal structure studies. The application of X-ray and electron diffraction techniques to structure studies has been compared in several books and articles on this subject. In this article some comparisons will be made of the results which can be obtained by these three techniques, and their advantages and disadvantages in particular applications will be outlined. The relatively small amount of work which has so far been carried out in the field of neutron diffraction will, of necessity, limit the scope of these comparisons, but it is hoped that they will show, in part at least, the significance of the new entry in the field of structure studies.

Characteristics of the Radiations

Although the radiations or particles with which we are here concerned, namely, photons, electrons, and neutrons, have widely different physical characteristics, they have the one property in common that there is associated with each a wave length which depends on the energy of the particular particle. The wave lengths which are useful in the study of crystal and molecular structure must be of the order of the distance between atoms in crystals or molecules in order that noticeable diffraction effects will be observed. Since atomic spacings are of the order of an angstrom, the useful wave length range will lie in the region from about 0.1 A to 10 A. With the proper choice of energy, X-rays, electrons, and neutrons can all be obtained with wave lengths lying in this region. Fig. 1 shows the relation between the energy and the wave length for these three radiations.

The nature of the sources and the intensity distribution as a function of wave length which can be obtained from these sources is very different for the three kinds of radiation. The radiation from an X-ray tube consists of the general radiation with a continuous distribution of wave lengths and the monochromatic line radiation which is characteristic of the target material. Both the general and the line radiation have been found useful in connection with the application of X-rays to structure studies, but if it had not been for the presence in X-rays of sharp monochromatic lines, a very serious handicap would have been placed on the technique, and much of the work which has been done would not have been possible. An appreciable fraction of the total energy from an X-ray tube is concentrated in these lines, and for many crystal structure studies this line radiation can be used directly without any further monochromatizing device being required. Where it is necessary to have a pure monochromatic source, as in experiments on the scattering by liquids and gases, balanced filters may be used or the line radiation may be reflected from a crystal and the general radiation thus eliminated. The general radiation from an X-ray tube is used in the application of Laue photography to structure studies.

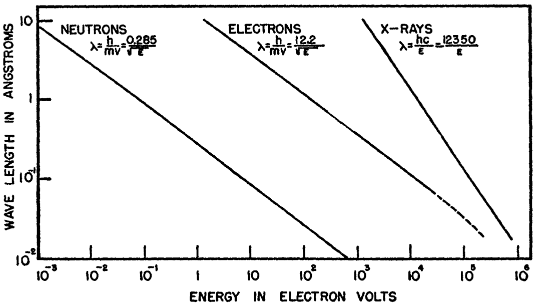


FIG. 1. Comparison of the relationship between particle wave length and energy for X-rays, electrons, and neutrons.

In electron diffraction studies the electron beam is universally obtained by the direct acceleration of the charged particles through electric potentials of the order of 30–50 kv, and this constitutes a monochromatic source of electrons within the limits of stability of the applied potential. Neutron sources, on the other hand, are essentially heterogeneous. In the chain reactor, which is by far the most powerful neutron source available, neutrons are produced in the fission process with wave lengths much too small for diffraction purposes. These neutrons are, however, slowed down in the moderating substance of the pile until they are in approximate thermal equilibrium with the atoms making up the moderator. A beam of such neutrons from a chain reactor is found to possess a nearly Maxwellian distribution of neutron velocities corresponding to a wave length distribution with a maximum intensity in the region of 1 A–2 A. The wave lengths in such a beam are in the desired region for diffraction experiments but, as such, their application would be restricted, as in the case of the general radiation from an X-ray tube, to techniques requiring a continuous distribution of wave length such as Laue photography. Monochromatic beams can, however, be obtained from the thermal beam by use of either a velocity selector or a crystal monochromator in which a narrow band is picked out of the continuous distribution.

Fig. 2 gives a comparison of the intensity distribution from X-ray, electron, and neutron sources. With slow neutrons only sources with a distribution of energies are obtainable. With electrons a monochromatic source of any desired wave length in the region of interest can be readily obtained. The radiation from an X-ray tube, on the other hand, gives both the general radiation with a distribution in energy and a wide choice of sharp monochromatic lines whose wave length depends on the target material.

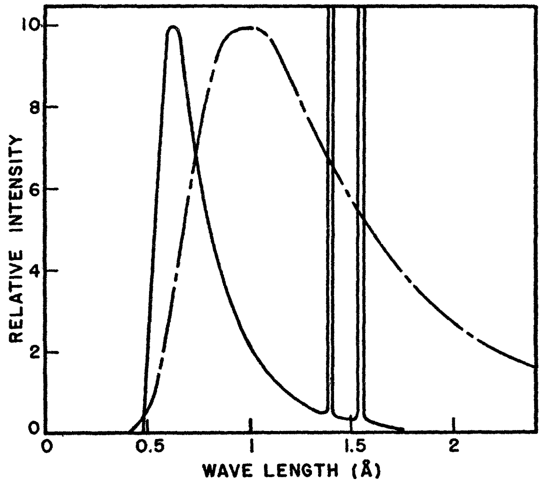


FIG. 2. The spectral distribution of radiation from various sources. The solid line represents the spectrum from a Cu target X-ray tube operated at 25 kv. The dashed line gives the approximate spectral distribution of neutrons from the Oak Ridge reactor.

The nature of the interaction of X-rays, electrons, and neutrons with individual atoms and nuclei is found to be very different for the three types of radiations. The scattering of X-rays by atoms takes place almost entirely from the electronic cloud surrounding the atomic nucleus, there being negligible scattering by the nucleus itself. Since the electrons are distributed over the atomic volume, which has a linear extent of about 1 A, and since this is of the same magnitude as the X-ray wave length, pronounced interference effects are to be expected in the scattering by individual atoms. This takes the form of an intensity reduction in the scattering at larger angles and is described by the conventional X-ray *form factor.* In the scattering of electrons by atoms, however, nuclear scattering is no longer negligible in comparison with the electronic scattering, so that additional interference effects are found for this case. The form factor for scattering of electrons is even more pronounced than it is for X-rays. As illustrations of this form factor scattering, Fig. 3 shows the decline in scattering amplitude with $\frac{\sin \theta}{\lambda}$ for the case of X-ray and electron scattering by copper atoms. In contrast, the amplitude of neutron scattering is shown as isotropic. This occurs because neutron scattering is caused overwhelmingly by interaction with the atomic nucleus, the neutron-electron interaction being usually negligible in comparison. The scattering is isotropic for such cases because the neutron wave length, being of the order of 10^{-8} cm, is so much larger than the physical size of the nucleus, which is of the order of 10^{-13} cm.

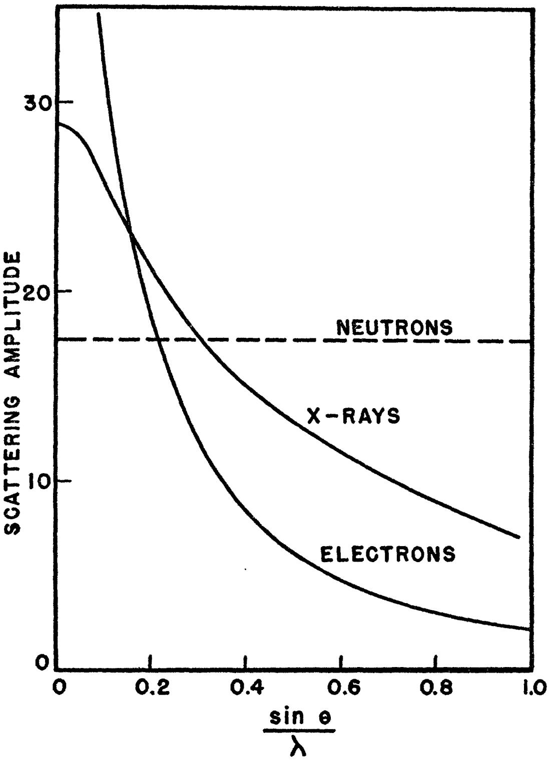


FIG. 3. Amplitude of scattering by copper atoms for various radiations.

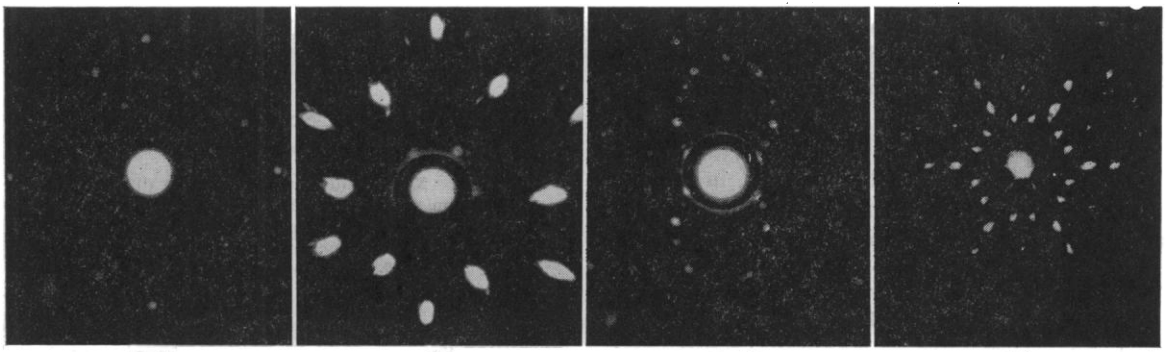
The form factors for X-rays and electrons represent the scattering amplitude for an atom relative to that for a single bound electron. The absolute scattering amplitudes for X-rays and electrons can be determined from the theoretically known scattering amplitude for a single electron. These theoretical scattering formulas have been well verified by scattering experiments. In the case of neutrons it is, however, not possible to make accurate calculations of scattering amplitudes, but they have been determined experimentally for a large number of nuclei. Scattering cross sections, which are proportional to the square of the scattering amplitudes, are of the same order of magnitude for X-rays and neutrons, but for electrons they are larger by a factor of several million. Table 1 lists the absolute scattering cross section per unit solid angle for X-rays, electrons, and neutrons for several elements. Since the cross sections for X-rays and electrons vary with scattering angle, they have been evaluated at the definite value of $\frac{\sin\theta}{\lambda} = 0.2$, while for neutrons this is not necessary, since the scattering by bound nuclei is isotropic.

TABLE 1

DIFFERENTIAL SCATTERING CROSS SECTIONS FOR VARIOUS SCATTERING CENTERS

	Neutrons	X-rays	Electrons
H	0.16	0.012	9.7×10^6
D	0.33	0.012	
C	0.38	0.48	320×10^6
O	0.33	1.5	260×10^6
Cl	1.04	6.7	$1{,}160 \times 10^6$
Cu	0.56	24	$2{,}070 \times 10^6$
Pb	0.79	240	$7{,}500 \times 10^6$

All values calculated for $\frac{\sin\theta}{\lambda} = 0.2$ and are in units of barns ($= 10^{-24}$ cm^2).



NaCl Be quartz Mg

FIG. 4. Laue photographs taken with NaCl, Be, quartz, and Mg. The former three were taken with neutron radiation; the latter, with X-rays.

In structure determinations the absolute scattering cross sections are not important as long as there is sufficient scattering by the sample. The relative scattering by the different atoms or nuclei in a crystal or molecule will be the determining factor in structure analysis. With X-rays and electrons the scattering by a hydrogen atom which has only a single electron will be very weak compared to the scattering by atoms of larger atomic number, since the amplitude increases about linearly with atomic number. With neutrons there is no regular variation of the scattering amplitudes from one element to the next, and hydrogen and deuterium have scattering cross sections comparable to other elements; hence, structure determinations involving these nuclei may be much more feasible with neutrons than with X-rays and electrons.

LAUE PHOTOGRAPHY

Since the neutron radiation available from reactor sources possesses a continuous distribution of wave lengths, it would seem most feasible to use this radiation with the Laue technique, which requires such a distribution. The Laue pattern, however, is of a two-dimensional nature, so that photographic detection of the pattern is necessary to make it of general usefulness and the photographic detection of neutrons presents problems not encountered in the X-ray and electron techniques. Neutrons, being nonionizing in their passage through matter, have practically no direct action on photographic emulsions. They can be detected indirectly, however, by placing some strong neutron-absorbing material either next to or combined with the emulsion, in which case the secondary radiations (electrons, α-particles, γ-rays) given off upon neutron capture may cause photographic action. The determination of the optimum conditions for such systems of activating substance plus emulsion has not yet been extensively explored, but by placing an indium sheet next to X-ray film, Laue photographs with neutrons have been obtained with exposure times of about 10 hrs. Some tests made with the addition of fluorescent screen material to the above activatorfilm combination have indicated this to be a promising technique, so that the required exposure time may be very much reduced—possibly into the range of X-ray exposure times of the order of 15 min.

Fig. 4 shows examples of neutron diffraction Laue patterns taken with single crystals of NaCl, Be, and quartz and, for comparison purposes, an X-ray diffraction Laue pattern taken with a magnesium crystal. Laue patterns are generally not taken with electrons because (a) extremely small crystals would be necessary because of the low penetrating power of electrons and (b) the heterogeneous nature of the required radiation (all wave lengths) is not easily obtained from electron sources. The quartz pattern of Fig. 4 shows the characteristic elliptical pattern of spots caused by reflections from the various planes passing through a particular zone axis. The spots in Laue patterns always fall in an elliptical array, but this may not always be as apparent as in the quartz pattern. The distorted appearance of the spots in the patterns for beryllium and magnesium is an indication of crystal imperfections and distortions in the metal crystals. The hexagonal symmetry in the metal patterns is clearly discernible.

DIFFRACTION BY CRYSTALLINE POWDERS

The Debye-Scherrer-Hull technique, in which a crystalline powder is illuminated with monochromatic radiation, has been widely used in diffraction studies.

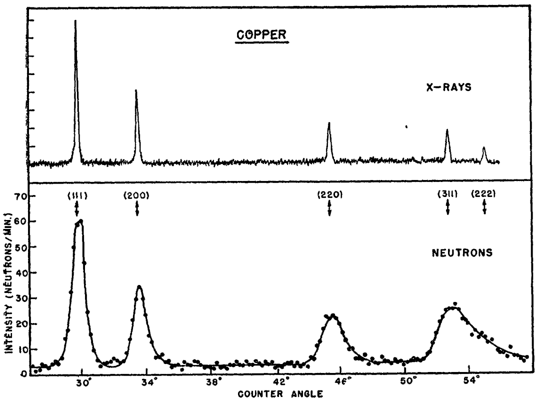


FIG. 5. X-ray and neutron powder diffraction patterns taken with copper powder. The lower resolution obtainable with presently available neutron sources is to be noted. Also of interest is the form factor decrease of X-ray intensity at the higher angles. The integrated intensities of the (311) and (111) neutron peaks are about equal, whereas with X-rays they are as 1 : 3.

This technique not only has the advantage of not requiring single crystals of the material to be examined, but offers as well the best procedure for obtaining absolute values of scattered intensity. With X-rays the characteristic radiation from a specific target material has been used as the source of monochromatic radiation, whereas with neutrons a crystal monochromator has been used to select a monochromatic slice of radiation from the continuous distribution of wave lengths present in pile radiation.

Figs. 5 and 6 show comparative X-ray and neutron diffraction powder patterns for examples of Cu and MnO. The X-ray patterns were kindly obtained for us by Dr. M. A. Bredig using a Philips Geiger-counter spectrometer, whereas the neutron patterns were obtained on the neutron diffraction powder spectrometer in use at Oak Ridge. Both spectrometers are of the automatic operation type. The patterns for Cu are very similar with two points of exception. First, it is to be noticed that the resolution in the X-ray pattern is about three times better than that shown for the neutron pattern. This is a consequence of the less refined geometry encountered in the neutron study as necessitated by the much lower intensity available. For the patterns produced by crystals possessing high symmetry where the diffraction lines are well separated, the limited resolution in the neutron pattern is not of serious consequence but for crystals of lower symmetry (rhombohedral, trigonal, etc.) this may be troublesome in showing unresolved peaks. A second point of interest in the Cu pattern is the form factor decrease of intensity at the higher angles for X-ray diffraction as compared to neutron diffraction.

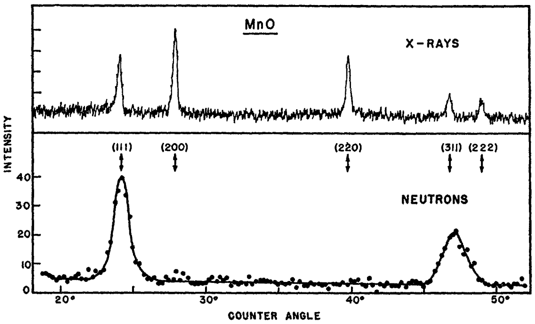


FIG. 6. X-ray and neutron powder diffraction patterns taken with MnO. The pronounced pattern differences are caused by the reversed phase of neutron scattering by Mn nuclei as compared to that by O nuclei. With X-rays, the scattering by the two atoms is of the same phase.

The diffraction patterns for MnO are included because they illustrate the case of polyatomic crystals and the phase reversal of neutron scattering for certain scattering centers. MnO crystallizes in a face-centered cubic structure (similar to that of NaCl), and the X-ray pattern for this substance is typical of this class of structures. The neutron diffraction pattern is markedly different, however, with peaks of high intensity at odd-indexed locations, while the even-indexed reflections are quite weak. This is an indication of the reversed phase of neutron scattering by manganese nuclei as referred to the scattering by oxygen nuclei. Theoretical considerations show that such a phase reversal is obtainable only in the close vicinity of a scattering resonance, and since this condition is met infrequently, only a few nuclei show the reversed scattering phase. No additional information on the structure of Cu or MnO is available from the neutron diffraction patterns, but the coherent scattering cross sections of neutrons by these nuclei have been determined from these patterns, and this is of interest as a nuclear physics study.

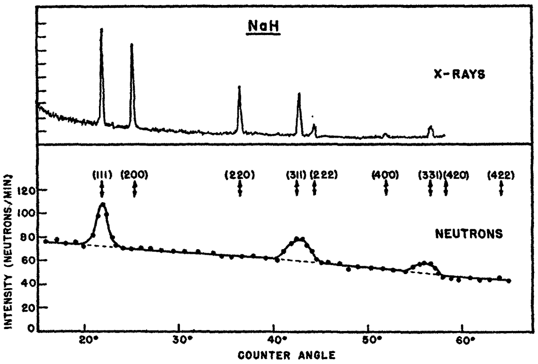


FIG. 7. X-ray and neutron powder diffraction patterns taken with NaH. The X-ray pattern is characteristic only of Na scattering, and the difference between the two patterns shows the influence of neutron scattering by hydrogen.

There appear to be many applications where the neutron techniques can usefully supplement the X-ray and electron diffraction procedures in the determination of crystallographic structures. As two examples of such applications, we shall mention studies on the determination of hydrogen atom positions in NaH crystals and on the order-disorder structure of Fe-Co alloys. Fig. 7 shows the X-ray and neutron diffraction patterns for a sample of NaH. Because of the very low X-ray scattering power of hydrogen compared with that of sodium, the X-ray pattern for NaH is characteristic only of the sodium positions in the crystal, and this has been determined to be of the face-centered cubic type. The pronounced difference between the X-ray and neutron patterns shows, however, that hydrogen scattering is contributing to the latter pattern, and a detailed study of the pattern intensities establishes that the structure is similar to that of NaCl. Thus, the hydrogen centers are located at positions in the crystal similar to those occupied by the chlorine centers in NaCl. From the neutron diffraction pattern of NaH it has been possible to evaluate the coherent scattering amplitude for neutron scattering by hydrogen, and, as shown in Table 1, this value is conveniently near those of other nuclei. The crystallographic location of hydrogen positions in more complex crystals (for instance, those of organic nature) should therefore be readily feasible with suitable neutron techniques. The structure of ice has been studied by the X-ray diffraction technique, and although it has been possible to locate the oxygen positions, this method gives no information about the location of the hydrogen atoms. A preliminary investigation of the structure of D_2O ice by neutron diffraction shows that considerable information on the location of the deuterium positions can be obtained by this technique.

In the study of the structure of alloys there is frequently encountered ordered solid solution in which one atomic species locates itself preferentially with respect to another species. In the system Cu_3Au for instance, heat treatment below 400° C produces an ordered structure in which gold atoms are located at the corners and copper atoms at the face-centered positions of a simple cube. Heat treatment at higher temperatures, however, produces a random substitution of gold atoms for the copper atoms in the normal copper lattice. The X-ray diffraction patterns for the ordered and disordered structures are materially different, and it is therefore easy to identify the individual structures. With the alloy FeCo, on the other hand, it is very difficult to distinguish between an ordered or disordered structure with X-rays, because the atomic structure factors of Fe and Co are so nearly alike. This similarity does not carry over to the neutron case, where the coherent scattering cross sections for Fe and Co are, respectively, 11 and 1.5 barns; in this case, therefore, it has been possible to identify the two structures. Fig. 8 shows neutron diffraction patterns for ordered and disordered samples of FeCo in which the additional diffraction features are to be noted for the case of the ordered sample. The ordered structure corresponds to a CsCl type of structure in which cobalt atoms are at the

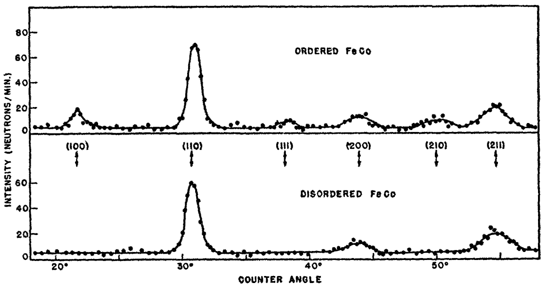


FIG. 8. Neutron powder diffraction patterns taken with samples of ordered and disordered preparations of Fe-Co alloys.

centers and iron atoms are at the corners of simple cubes.

Scattering by Gases and Liquids

Measurements of the angular dependence of the scattering of X-rays by monatomic gases give the atomic scattering factors (see Fig. 3) from which the average electron distribution in the atoms can be calculated.

Similar measurements with diatomic gas molecules constitute a direct method for measuring the distance between atoms in the molecule. Such measurements have been made with X-rays and with electrons, but so far they have not been made with neutrons because of lack of sufficient intensity. A rough comparison of the X-ray scattering curve for a diatomic molecule with the corresponding curves to be expected with neutrons can be made by reference to the well-known curves due to Debye (Fig. 9). The lower curve corresponds approximately to the X-ray case where the scattering electrons are distributed within a volume comparable in size to the distance between atoms, while the upper curve, which is calculated for point scattering centers, corresponds more nearly to the neutron case in which the atomic nuclei are responsible for the scattering.

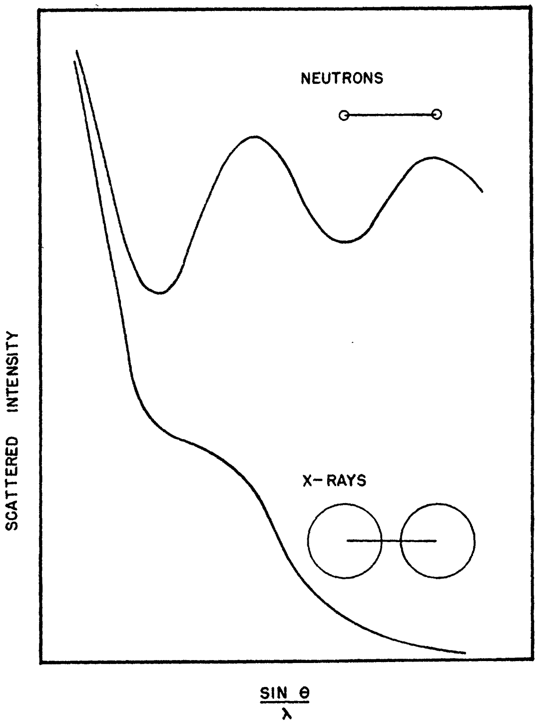


Fig. 9. Scattering curves for a diatomic molecule as calculated by Debye. The case where the atomic dimensions are comparable to the separation characterizes the X-ray scattering by a gas, whereas the case of point scattering corresponds to that expected with neutrons.

As the molecules to be studied by the diffraction technique become more complex, the data become more difficult to interpret, and a unique evaluation of the intermolecular spacings may not be possible. A rather simple polyatomic molecule which has been thoroughly studied by both the X-ray and electron diffraction methods is CCl_4 in the vapor state. A comparison of the coherent scattering of X-rays, electrons, and neutrons by CCl_4 will be made to illustrate the rather marked differences in the nature of the scattering curves to which the three radiations give rise. Fig. 10 shows the theoretical scattering curves for CCl_4 vapor for X-rays, electrons, and neutrons on an arbitrary scale. The X-ray and electron curves have been verified experimentally, while the neutron curve is calculated from the measured coherent scattering amplitude for carbon and chlorine. As one proceeds from electrons to X-rays to neutrons, the farther out peaks become more pronounced because of the nature of the scattering functions shown in Fig. 3. The sharper peaks which should be obtained with neutrons may lead to a higher resolving power for this radiation in molecular structure determinations.

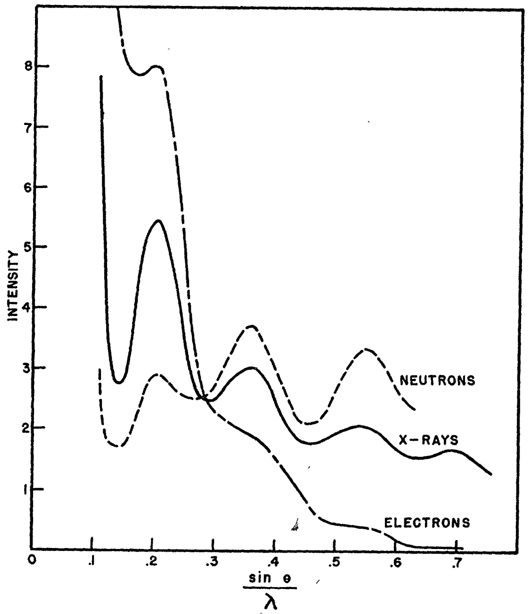


Fig. 10. Theoretical scattering curves for CCl_4 vapor for X-rays, electrons, and neutrons. The former two curves have been verified experimentally, while the latter has been calculated using the known neutron scattering amplitudes for carbon and chlorine.

Several studies have been made of the scattering of X-rays by CCl_4 in the liquid state. In this case there are, in addition to the interference effects between the various atoms in the molecule, the effects of interference between waves scattered by atoms in adjacent molecules. Fig. 11 shows an experimental

X-ray scattering curve for liquid CCl_4 and also a corresponding curve recently obtained for neutron scattering. The relative characteristics of the neutron and X-ray curves are seen to be similar to the corresponding curves for scattering by gaseous $C\ Cl_4$. Fourier analyses of the X-ray scattering data have given the spacings of the atoms in the molecule and also some information regarding the closer spacings for atoms in neighboring molecules. The neutron curve has not yet been determined with any great precision, and there remain some unsolved interpretative problems, but at a later date it will be interesting to compare the results of a Fourier analysis of the X-ray and neutron scattering curves.

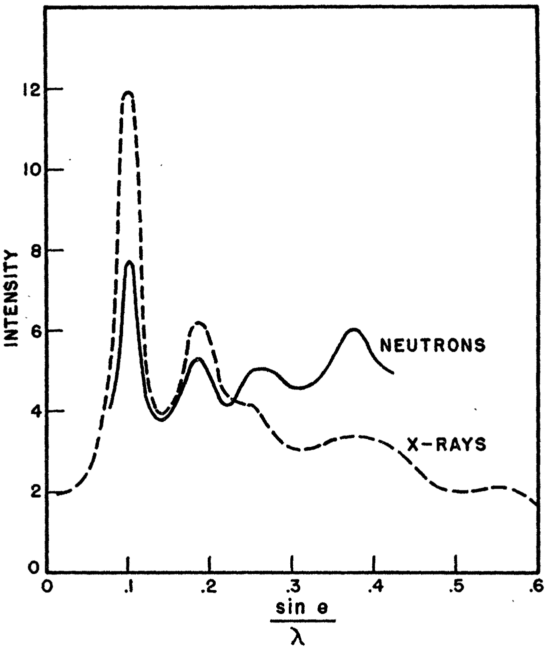


FIG. 11. Experimental scattering curves for liquid CCl_4 obtained with X-rays and neutrons.

CONCLUSIONS

The newly developing field of neutron diffraction would appear to have advantages over the older fields of X-ray and electron diffraction in some problems involved in the determination of crystal and molecular structures. The most important application for which this seems to be the case is in connection with the location of hydrogen or deuterium positions. So far, only very simple examples of such determinations have been carried out, but from these studies it would seem that there is no serious obstacle in the way of extending the technique to more complicated cases, especially where deuterated compounds can be used. If this is the case, neutron diffraction may become a very useful tool in the study of the structure of organic compounds. It must be borne in mind, however, that really rapid progress along this line cannot be expected, since in any case complicated structure determinations are very time-consuming problems; also, the very limited facilities for work in this field which result from the requirement of a chain-reacting pile as a source will make progress less rapid than in the corresponding fields of X-ray and electron diffraction, for which adequate sources can be procured by any laboratory.

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