Review

Local Structure and Dynamics of Functional Materials Studied by X-ray Absorption Fine Structure

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Abstract: X-ray absorption fine structure (XAFS) is a powerful technique used to analyze a local electronic structure, local atomic structure, and structural dynamics. In this review, I present examples of XAFS that apply to the local structure and dynamics of functional materials: (1) structure phase transition in perovskite PbTiO_3 and magnetic FeRhPd alloys; (2) nano-scaled fluctuations related to their magnetic properties in Ni–Mn alloys and Fe/Cr thin films; and (3) the Debye–Waller factors related to the chemical reactivity for catalysis in polyanions and ligand exchange reaction. This study shows that the local structure and dynamics are related to the characteristic function of the materials.

Keywords: XAFS; XMCD; Debye–Waller factor; structure and magnetic phase transition; magnetic alloys; chemical reactivity

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1. Introduction

Symmetry is one of the most important concepts in natural science. Symmetry lies at the heart of fundamental laws of nature as an important tool for understanding the properties of complex systems, including condensed matter physics, materials science, and technology. The concept of symmetry plays an important role in the phase transition, exotic electronic structure, magnetic structure, and chemical reactivity in condensed matters and chemical systems.

X-ray absorption fine structure (XAFS), which has been developed in recent years accompanying the synchrotron radiation source, is becoming a powerful technique that is used to study the local atomic structure, electronic structure, and structural dynamics of ferroelectric and magnetic materials, semiconductors, molecules, and gas-phase systems. XAFS is a hybrid technique that can be used to study both the structure and electronic state, which is strongly correlated with symmetry in condensed matters. I discuss the physical properties and chemical reactivities of multiple functional materials from the symmetry point of view, which can be a key concept of recent industrial innovation.

The history of XAFS began in the 1970s with the treatise of Lytle, Sayers, Stern [1]. Before the 1920s when the fine structure on X-ray absorption spectra was discovered, many researchers, including Japanese scientists, struggled to interpret its behavior [2,3]. This can be recognized as the starting point of XAFS when considering the physical meaning, and it led to a structural analysis of the materials. Recently, accompanying the development of synchrotron radiation sources and theoretical research, the XAFS technique has seen considerable advances. There are fewer limitations in the measurement setup because the X-ray absorption transmission technique is simple. XAFS is applicable to structure studies of solid, liquid, gas phase, thin films and nanoparticles because the atomic long-range order is not required. XAFS provides local structure information because of the relatively small electron mean free path emitted during the X-ray absorption process. These two characteristic features make XAFS a widely applicable technique, commonly being applied to the following: crystalline and non-crystalline samples, amorphous liquid and solutions, nanoparticles, surfaces, thin films, etc. [4–6]. Additionally, XAFS is an element and electron shell-selective by choosing the appropriate absorption edge. XAFS can be divided into

two parts: XANES (X-ray absorption near-edge structure) and EXAFS (Extended XAFS). EXAFS includes information about the local structure around the X-ray absorption atom as radial distribution because of the simple theoretical interpretation. On the other hand, the origin of XANES is more complicated than that of EXAFS and has rich information on the electronic structure, valence, and 3D local structure. One of the parameters of the EXAFS signal affected by thermal vibration and structural disorder, the so-called Debye–Waller factor, involves structure dynamics and disorders.

In this paper, I discuss examples of XAFS studies applied to functional materials in which symmetry, or symmetry breaking, plays an important role in the origin of their functions. Section 2 shows a brief introduction of the XAFS method and analysis. In Section 3, structural phase transition in highly symmetric perovskite-type PbTiO_3 and FeRh(Pd) systems with CsCl-type structures are presented. Section 4 shows the application of a circularly polarized X-ray source to a magnetic alloy of Ni–Mn and multilayer of Fe/Cr. Section 5 shows the application of Debye–Waller factor analysis to chemical reactivities, where the chemical reactivity as a catalyst of Mo polyanion and ligand exchange reaction of 3d metal ion in water are discussed.

2. Methods and Analysis

XAFS is an analysis of the fine structure on the absorption edge in X-ray absorption spectra. The basic measurement mode is a transmission mode using, for example, ionization chambers to measure the photon flux before and after the sample. XAFS can also be measured in fluorescence (using semiconducting detector) or electron-yield mode; these techniques are well suited to study thin films, dilute elements, or surface structure. EXAFS formalism is well defined and simple within a single scattering theory [7], but XANES formalism is complicated and uses band calculation and molecular orbital schemes or multiple scattering calculations [8].

From the EXAFS analysis, the interatomic distance from the X-ray absorbing atom to the nearest neighboring atoms as a radial distribution, their coordination numbers, and thermal and structural fluctuation at the distances (so called Debye–Waller factor) can be obtained as the structural information. The XANES region is sensitive to the electronic state of X-ray absorbing and surrounding atoms. XANES is also sensitive to the 3D structure, because the multiple scattering effects are important with long photoelectrons, causing a mean free path at such low-energy photoelectrons.

The Debye–Waller factor in EXAFS includes information from thermal dynamics and structure disorders. Cumulant expansion analysis reveals the anharmonic effect of the thermal vibration and structure disorder [9,10]. To obtain the several order cumulants, there are two types of theoretical pictures: the field theoretical method for the small anharmonic effect and the path integral technique, which is applied to a large anharmonic effect, e.g., double-well potential.

3. Local Structural Change in Phase Transitions in Perovskites and Magnetic Alloys

In this section, I discuss two types of structural phase transition in PbTiO_3 and FeRh(Pd) magnetic alloys. These two examples have long been studied, and their industrial application is becoming important today. The first example is perovskite-type PbTiO_3 , in which, among the same type of perovskites, the largest distortion on the tetragonal to cubic transition is known to occur. The second example is the structural change observed in the transition from antiferromagnetic to ferromagnetic in FeRh and FeRhPd alloys, which show a large magnetocaloric effect near room temperature.

3.1. Structure Phase Transition in Perovskite-Type PbTiO_3

Structural phase transition is an interesting subject in basic physics, and it has recently attracted industrial attention. Perovskite-type materials are important in this phase transition system. In basic physics, these phase transitions are treated as being deeply related to symmetry breaking. The phase transition mechanism in PbTiO_3 has been well studied

by diffraction techniques because of the large distortion of ions along the c -axes in the tetragonal phase. Two types of phase transition have been proposed: “displacive type” and “order–disorder type”. The displacive type is connected to the actual atomic displacement between two phases. The displacive transition generally involves *soft mode*, where the frequency of the atomic vibration tends to zero at the critical temperature. However, with the order–disorder type, local atomic displacement is conserved between two phases, but the direction of distortion changes to be randomly oriented. While the diffraction technique based on long-range order (LRO) cannot be easily and clearly distinguished by these two types of transitions. XAFS based on short-range order (SRO) could show local distortions. For example, in the cubic phase, the bond distance of three directions (x, y, z) is the same in the diffraction technique, but XAFS shows different distances in the case of order–disorder transition. From the original neutron and X-ray diffraction study, the so-called displacive transition is proposed in the transition between the tetragonal and cubic phase in PbTiO_3 , in which the relative displacement of ions disappears at a higher temperature phase. Recently, from high-resolution X-ray diffraction studies, the Pb–O bonds show considerably strong covalency in tetragonal PbTiO_3 , while those bonds in the cubic phase are ionic [11]. However, XAFS is sensitive to local electronic and atomic structures, and it is useful for the detection of such a local atomic displacement. Figure 1a shows the temperature dependence of the area of pre-edge peak (A, narrow peak at 4968 eV) on Ti K-edge for PbTiO_3 [12]. The pre-edge A is generated from weak quadrupole transition in the $1s-3d$ state because dipole transition is forbidden. If the p -state from the ligand O atom hybridizes to the d -state of Ti, then a strong pre-edge peak is observed. The mixing of the p -state strongly depends on the symmetry around Ti atom; when it is more deviated from O_h symmetry, the peak becomes larger, so the peak intensity is used as an indication of symmetry. The area of peak A decreases from low temperature to 763 K, but the area value is still largely higher than 0, even in the cubic phase (higher than 763 K).

This phenomenon is also recognized in the interatomic distances obtained from EXAFS analysis. Figure 1b shows the temperature dependence of the interatomic distances for three types of Pb–O pairs obtained from Pb L_{III}-edge EXAFS [13]. There are completely separated by three different Pb–O distances in the tetragonal region (less than 763 K). In these three types of atomic pairs, the longest pair of Pb–O(3) shows the same behavior as that of the area of peak A shown in Figure 1a. It is noted that there are still three different interatomic distances, even in the cubic phase (higher than 763 K). Moreover, the symmetry around the Ti atom is not completely the same as that of the Pb atom. However the distortion of O(3) atoms related to the Pb atom induces the symmetry breaking around the Ti atom. This result shows that there is local distortion, even in the cubic phase as similarly shown in Figure 1a, in which distortion peak A still exists in the cubic phase. The distortion in the cubic phase deduces the order–disorder type transition. As a result, the structural phase transition in PbTiO_3 is hybrid type, where the longest Pb–O(3) along the c -axis is displacive type, and Pb–O(1) and Pb–O(2) show the order–disorder-type transition. Figure 1c shows the temperature dependence of the Debye–Waller factor for the Pb–O(3) atomic pair. The softening behavior, which is the feature of displacive-type transition, can be clearly observed, and this cannot be found in other Pb–O(1,2) pairs [12]. The EXAFS revealed characteristic features in the longest Pb–O(3) atomic pairs in the structural phase transition of PbTiO_3 .

Figure 1. (a) Temperature dependence of the area of the pre-edge peak (narrow peak at 4968 eV) on Ti K-edge XANES (inset shows the XANES profiles around the pre-edge peak A). (b) Temperature dependences of interatomic distances of three types of Pb–O(1,2,3) in PbTiO₃ obtained from the Pb L_{III}-edge EXAFS. (c) Temperature dependence of the Debye–Waller (σ^2) factor of Pb–O(3) atomic pair in PbTiO₃ obtained from Pb L_{III}-edge EXAFS [12].

3.2. Structure Phase Transition in FeRh and FeRhPd Magnetic Alloys

FeRh magnetic alloys exist as a chemically ordered phase near the equiatomic composition, and the ordered alloy shows a first-order phase transition from an antiferromagnetic (AFM) to a ferromagnetic (FM) phase around $T_p = 370$ K [14]. This system has also long been studied by those with an interest in basic physics. However, it is still a hot topic because of the application to the magnetic refrigerator [15]. Accompanying the magnetic transition in this temperature region is a sharp thermal expansion that can be observed, but there is no satisfied model in which either magnetic transition affects the structural one or vice versa. It is still an open question similar to the “egg or chicken” problem. Figure 2a,b show the temperature dependence of the Fourier transform (FT) for Fe K-edge and Rh K-edge EXAFS for Fe_{50.4}Rh_{49.6}, respectively. After the detailed fitting analysis, the atomic distances can be obtained, and their temperature dependences are shown in Figure 2c. I assume that the bcc structure is preserved over the transition, and Fe–Rh (or Rh–Fe) is plotted by times $2/\sqrt{3}$ to compare Fe–Fe (or Rh–Rh). The behavior of Fe–Fe is almost the same as that of Rh–Rh. It is strange that the lattice distance of Fe–Rh (or Rh–Fe) is shorter than that of Fe–Fe (or Rh–Rh) [14]. A similar discrepancy has been observed in the XAFS study of FeRh thin films [16]. The behavior of Fe–Fe (or Rh–Rh) and Fe–Rh (Rh–Fe) is different. While the sharp expansion for Fe–Rh (or Rh–Fe) starts at 250 K (T_1) and finishes at 350 K (T_2), that for Fe–Fe (or Rh–Rh) finishes at 400 K (T_3). To date, the mechanism of this interesting phenomenon remains unsolved, but one interpretation was proposed that the local distortion to (111) direction starts at T_1 and finishes at T_2 ; in the distorted phase, Fe–Rh (or Rh–Fe) distance is shorter than Fe–Fe (or Rh–Rh) distance because of the EXAFS two-shell fit. At the temperature range between T_2 and T_3 , the unchanged distortion shows only thermal expansion [14].

Figure 2. EXAFS Fourier transforms of (a) Fe K- and (b) Rh K-edge EXAFS, and (c) temperature dependences of interatomic distances obtained from EXAFS curve fitting for ordered Fe_{50.4}Rh_{49.6} alloy. The interatomic distance of Fe–Rh (or Rh–Fe) is plotted by times $2/\sqrt{3}$ to compare it with that of Fe–Fe (or Rh–Rh) [14].

When a small portion of Rh atoms are replaced by Pd atoms, the magnetization increases and T_p shifts to a lower temperature. Fe and Pd K-edge EXAFS for $\text{Fe}_{49.7}\text{Rh}_{47.4}\text{Pd}_{2.9}$ and $\text{Fe}_{48.3}\text{Rh}_{46.8}\text{Pd}_{4.9}$ alloys were discussed as follows: (1) local distortion as found in FeRh, and (2) the role of Pd atoms in changing the magnetic properties [17]. Figure 3a,b show $k\chi(k)$ and the Fourier transform of Pd K-edge EXAFS for $\text{Fe}_{49.7}\text{Rh}_{47.4}\text{Pd}_{2.9}$ alloys for several temperatures. The original FeRh alloy has a bcc-CsCl structure, and Rh atoms are considered to be replaced by Pd atoms in $\text{Fe}_{49.7}\text{Rh}_{47.4}\text{Pd}_{2.9}$ alloys. The interatomic distances of Fe–Rh and Fe–Fe obtained from the Fe K-edge XAFS analysis for $\text{Fe}_{49.7}\text{Rh}_{47.4}\text{Pd}_{2.9}$ and $\text{Fe}_{48.3}\text{Rh}_{46.8}\text{Pd}_{4.9}$ are about 0.02 Å longer than that from $\text{Fe}_{50.4}\text{Rh}_{49.6}$ [17]. These results can be estimated from the lattice constant of XRD, which means that the local structure around Fe atoms from XAFS is almost the same as the average structure from XRD. However, the interatomic distances of Pd–Fe and Pd–Rh obtained from the Pd K-edge XAFS analysis for $\text{Fe}_{49.7}\text{Rh}_{47.4}\text{Pd}_{2.9}$ and $\text{Fe}_{48.3}\text{Rh}_{46.8}\text{Pd}_{4.9}$ are about 0.04 Å longer than that from $\text{Fe}_{50.4}\text{Rh}_{49.6}$ [17]. This result means that the local structure around the Pd atom is more expanded than that around Rh atoms in FeRhPd alloys. The expansion around Pd atoms is expected to play an important role in the characteristic magnetic properties in FeRhPd, e.g., decreasing transition temperature, T_p , as Pd doping.

Figure 3. (a) $k\chi(k)$ and (b) Fourier transforms of Pd K-edge EXAFS for $\text{Fe}_{49.7}\text{Rh}_{47.4}\text{Pd}_{2.9}$ alloy for several temperatures. The result of Pd metal (black line) is also included.

4. Study of Local Structures of Magnetic Alloys and Thin Films

In this section, I discuss the application of magnetic EXAFS and X-ray magnetic circular dichroism (XMCD) to magnetic alloys of Ni–Mn and a multilayer of Fe/Cr, in which atomic ordering is important to characteristic magnetic features.

4.1. Magnetic EXAFS for Ni_3Mn Alloys

Ni_3Mn magnetic alloys have also been a long-studied system, where they have a coupling between the structure disorder and magnetic properties. I studied the magnetic EXAFS for Mn using circular polarized X-ray, and the following is the discussion of the effect of atomic arrangement in order–disorder couplings to magnetic properties [18,19]. In the magnetic EXAFS, the amplitude is proportional not only to the coordination number but also to the magnetic moment of X-ray absorbing and photoelectron scattering atoms because of spin–orbit coupling. Figure 4 is the Fourier transforms for Mn K-edge of (a) conventional EXAFS and (b) magnetic EXAFS for $\text{Ni}_{0.75}\text{Mn}_{0.25}$ alloy, which was heat-treated at 693 K in 500 hours to order the atomic arrangement ($S = 0.78$) [18]. In the ordered Ni_3Mn alloy, the Mn atom has a large magnetic moment (about $3.15 \mu_B$ [18]) and is located at the second nearest neighbor (NN) and fourth NN from the X-ray absorbing Mn atom. The FT modulus peak intensity of the second and fourth NN in Figure 4b becomes larger than that in Figure 4a because of the large magnetic moment of Mn. From the ratio of the intensities of the first (Ni) and second (Mn) peaks, the ratio of the magnetic moment

can be evaluated. Table 1 shows the result of magnetization, LRO of the sample, and the ratio of the magnetic moment (Mn/Ni) for several annealing conditions. From our band calculation, the theoretical value of the magnetic moment ratio, Mn/Ni, is 5.2, which is close to the magnetic EXAFS result for the 500 h annealing sample (Mn/Ni = 5.9) [19]. The experimental result shows that the Mn/Ni magnetic moment increases for a longer annealing time, or further ordering proceeds. In another study, from giant magnetoresistance (GMR) experiments [20], the cluster size of the ordered ferromagnetic Ni₃Mn phase becomes larger for a longer annealing time, or further ordering proceeds. These results indicate that the magnetic moment of Mn atoms in the highly ordered Ni₃Mn phase is larger than that in the less ordered phase.

Figure 4. Mn K-edge Fourier transforms of (a) non-magnetic and (b) magnetic EXAFS for ordered (500 h annealing) Ni_{0.75}Mn_{0.25} alloy. Dotted lines are the theoretical calculation spectra.

Table 1. Sample magnetization, long-range order (LRO), and the ratio of the atomic magnetic moment of Mn/Ni for the samples with several annealing times.

Anneal (h)	Magnetization (emu/g)	LRO	Ratio Mn/Ni
50	50.0	0.44	3.5
100	56.4	0.55	4.3
500	85.9	0.78	5.9

4.2. XAFS and XMCD Study for Cluster-Layered Fe/Cr Films

For the Fe/Cr multilayered structure, GMR was discovered in 1988 [21,22]. In such multilayer structures and granular thin films with ferromagnetic nanoparticles, the correlation between magnetic and transport properties is actively studied [23–25]. In 2006, a minimum point (~170 K) in the temperature dependence of the resistivity (see Figure 5a) was observed in cluster-layered Fe/Cr nanostructures [26]. In this ultrathin film, the small portion of Fe exists as a ferromagnetic cluster in Cr and indicates superparamagnetic features but no GMR behavior. Local magnetic and atomic structures of cluster-layered Fe/Cr thin films were studied by Fe L_{II,III}-edge XMCD and Fe K-edge EXAFS, respectively [27]. Figure 5b shows the temperature dependence of the total magnetic moment obtained from the sum rule for Fe L_{II,III}-edge XMCD of Al₂O₃/Cr(70 Å)/[Fe(1.2 Å)/Cr(10.5 Å)]₃₀/Cr(12 Å). The direction between the normal direction of the sample film surface and X-ray beam direction, θ , is set to 55 degrees. The magnetic moment of Fe atoms decreases as the temperature increases and disappears above the temperature of minimum resistivity.

From the Fe K-edge EXAFS, it appears that the local structure of this film around Fe atoms for Al₂O₃/Cr(70 Å)/[Fe(1.2 Å)/Cr(10.5 Å)]₃₀/Cr(12 Å) is rather disordered, which can be related to the magnetic fluctuations estimated from the theoretical treatment of the temperature dependence of magnetic moments [27].

Figure 5. Temperature dependence of relative resistivity for several magnetic fields (a) and that of the total magnetic moment of Fe atoms obtained from XMCD at $\theta = 55$ degrees (b).

5. Structure Dynamics in Chemical Reaction Systems

In this section, I discuss the structural disorder and dynamics in chemical reaction systems via an analysis of the Debye–Waller factor. The first example is Mo hexamer polyanion. The large fluctuation of the bond distance of the bridging Mo–O–Mo bond is related to chemical reactivity as catalysis. The second example is the ligand exchange reaction, in which an anharmonic potential (or dissociation energy) of 3d metal ion and ligand H₂O is obtained from the cumulant analysis of EXAFS. This is related to the ligand exchange reaction rate.

5.1. Structural Disorder in Polyanion of Mo and W

Mo and W produce the same type of polyanions, such as $M_6O_{19}^{2-}$ (see Figure 6a), and show interesting catalytic properties. These Mo and W polyanion hexamers are highly symmetric structures, and their EXAFS shows interesting behavior [28,29]. Figure 6b shows the EXAFS Fourier transform for $M_6O_{19}^{2-}$ ($M=Mo$ and W). It is interesting that while the FT peak intensities of Mo–Mo and W–W are similar, as expected from the structure data, those of Mo–O and W–O are different—W–O seems to be normal, but Mo–O is unnaturally small, although they have a similar symmetric structure. To investigate the reason, I measured the temperature dependence of the Debye–Waller factor and analyzed individual atomic pairs. Figure 6c,d show temperature dependence of the Debye–Waller factor for $Mo_6O_{19}^{2-}$ and $W_6O_{19}^{2-}$, respectively. While there are three types of M–O bonds in the hexamer, only the Debye–Waller factor of the bridging Mo–O2 is abruptly large. More interestingly, the temperature inclination of Mo–O2 is the same as that of other atomic pairs, but the absolute value of this bond is large. This means that the structural disorder of the Mo–O2 bond is abnormally large in comparison to that of other atomic pairs. The Jahn–Teller effect of the Mo–O2 bond has been reported and suggests an alternative Mo–O=Mo bond distance in $Mo_6O_{19}^{2-}$ [30]. This larger disorder in bridging the Mo–O2 bond may come from the Jahn–Teller effect and should affect the high chemical reactivity of this species.

5.2. Ligand Exchange Reaction in 3d Transition Metal Ions in Water

Finally, I introduce the EXAFS application to ligand exchange reactions [31,32]. It is known that 3d transition metal ions exist as hydrated $M(H_2O)^{n+}$ ions in the water solutions, and ligand H₂O molecules continuously exchange with water H₂O. These exchange rates are widely distributed from 10^{-6} s to 10^8 s. I obtained a harmonic potential of M–(OH₂) from the temperature dependence of the Debye–Waller factor in EXAFS for M–O pairs using the relation between the anharmonic potential and higher order cumulant of the thermal factor. As the anharmonic potential of M–(OH₂), simple Morse potential was assumed, such as

$$V(x) = D(e^{-2\alpha x} - 2e^{-\alpha x})$$

Figure 6. (a) Molecular structure of $M_6O_{19}^{2-}$ (M=Mo, W) compound, (b) EXAFS Fourier transforms of Mo K- and W LIII-edge EXAFS for $M_6O_{19}^{2-}$ (M=Mo for a solid line, W for dashed line), (c) temperature dependence of the Debye–Waller factors for M–O and M–M for $Mo_6O_{19}^{2-}$, and (d) that for the $W_6O_{19}^{2-}$ compound (O1: terminal oxygen, O2: bridged oxygen, O3: center oxygen). Reprinted with permission from [29].

From the temperature dependence of the second- and third-order cumulants, dissociation energy, D , and the anharmonic parameter, α , can be obtained [32]. Figure 7 shows the plot of D values as a function of the logarithm of the ligand exchange reaction rate. There is a clear correlation between D and the exchange rate. In Figure 7, $\times$ represents the result obtained from molecular orbital calculation [33]. The experimental result from EXAFS is slightly smaller than the theoretical one, but their inclinations are similar. It was shown that the ligand exchange rate is strongly related to the anharmonic metal–ligand potential.

Figure 7. Plots of the dissociation energy, D , of a water molecule obtained from EXAFS anharmonic analysis as a function of the water exchange reaction rate (•). The result from the molecular orbital calculation is also presented (×). Reprinted with permission from [32].

6. Conclusions

In this review, XAFS applications to local structures and dynamics of functional materials were presented. The materials discussed here are classified into three types of subjects: (1) local structure change in phase transitions of perovskites and magnetic alloys, (2) study of local structures of magnetic alloys and thin films, and (3) structure dynamics in chemical reaction systems. These physical and chemical properties are strongly related to atomic displacement or arrangement.

In structure phase transition, XAFS is sensitive to specific evolutions, such as soft-mode evolutions or distortion in a specific direction. Magnetic EXAFS and XMCD studies using circular polarized X-ray are sensitive to the magnetic moment of individual atoms in the alloys and thin films. The Debye–Waller factor in EXAFS, which includes the effect of structural distortion and atomic vibration, is connected to the chemical reactivity.

It is shown that XAFS is a local probe and that it is sensitive to a local change in atomic and magnetic structure and structural dynamics, which affect the functions of the materials. Although XAFS has the advantage of allowing for the study of local structure, physical and chemical properties are related to not only SRO but also LRO. In the future, XAFS will continue to be an attractive research technique complementary to the diffraction techniques in material sciences.

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