X-Ray Magnetic Absorption and Scattering (XMAS)

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1 . Introduction

Understanding of magnetic property and structure in magnetic materials forms a wide field of research interesting not only from a fundamental point but also from a practical point. Advantages in brilliance and polarization of 3rd generation synchrotron radiation (SR) open out a new field in magnetism differing from neutron magnetic scattering. In particular, this is characterized by separation of spin and orbital features, high *k*-resolution, and resonant enhancement. For the purpose of such research, spectroscopy and diffractometry using linearly or circularly polarized X-rays are useful technique and will be realized on BL-39XU in the photon energy range from 5 to 25 keV. This end station is composed mainly of a diffractometer and a phase retarder assembly.

2. Experimental Utility

Figure 1 shows a schematic design of the 3-circle diffractometer installed on a large *y*-*z* translation stage. Another 4-circle goniometer mounted on the 2θ-arm functions as a polarization analyzer assembly. The scattered X-rays are separated into the a- and IE-polarization components to specify the scattering matrix elements originating from magnetic property [1]. The ω-circle can simultaneously carry the equipment of magnetic field and low-temperature. An additional ϖ-arm is available for a free rotating fluorescence detector or for sample to be independently orientated of the direction of magnetic field.

A phase retarder assembly, which will be placed at the most up=stream in the hutch, is indispensable either to generate circular polarization (λ/4-phase plate) or to produce vertical linear polarization (λ/2-phase plate) [2,3]. A synthetic diamond (001) crystal will be operated near the 111 asymmetric reflection in Laue geometry. This system has two advantages: Control of degree of polarization and alternation of polarization states. The polarization tunability is prerequisite for characterizing magnetic effects in both spectroscopy and diffractometry. Switching of polarization can remove restrictive conditions on the applied magnetic field, and allows us to make experiments in polarization-modulation mode, resulting in an improvement in data accuracy.
Equipment for sample environment in the initial stage consists of an electromagnet up to 1 Tesla and a He-gas closed cycle refrigerator cooling down to 5 K. To introduce the experiments under extreme conditions, a superconducting magnet up to 10 Tesla and a diamond anvil cell up to 10 GPa will be installed in near future. Detector includes a Si(Li) SSD, scintillators, and ionization chambers. Since 2-dimensional imaging of magnetic structure is useful for characterizing practical materials, position sensing detector such as CCD camera will be proposed. To increase flexibility of sample orientation~ an additional goniometer with χ and ϕ-circles will be equipped on the ω-circle of the diffractometer. Several devices for sample preparation and characterization will be installed in the sample preparation room.

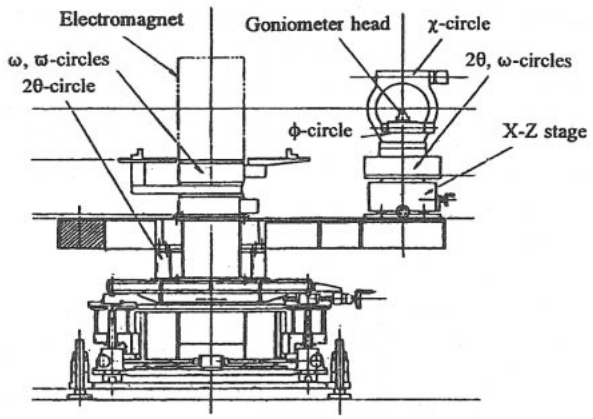

Fig.1 Schematic view of the diffractometer.

3. Scientific Applications

Our objective is to understand magnetic states and magnetic structure in detail through the interaction between magnetic electrons and the polarized X-rays. The information, such as magnitude, distribution, and arrangement of spin and orbital angular momenta, will lead us to advanced understandings of magnetic property in transition metal (M) and/or rare-earth (R) magnetic materials.According to the polarized

X-rays to be used, our research subjects are classified into two categories: (1) Spectroscopy and diffractometry using circular polarization,
(2) Diffractometry using linear polarization.

3.1 Spectroscopy and diffractometry using circular polarization

3.1.1 Magnetic circular X-ray dichroism (MCXD)

This subject has attracted extensive interest from the viewpoint of material science. However, the electronic states related to *K* or *L*-absorption edge are of delocalized electrons, *i.e.* 4*p* and 5*d*, so that it is indispensable for associating with calculations to interpret the spectrum. Several theoretical approaches have been recently succeeded in qualitative explanation. The agreement between experiments and calculations is making progress in basic understanding of electronic states. In view of this state, this technique will develop into systematic study with higher efficiency, statistical accuracy, and resolution.

The following materials will be treated in connection with basic issue in magnetism: (1) M 3*d*-electronic states in ligand fields (M compounds), (2) dipole and quadrupole transitions, magnetic local structure (R-M amorphous thin films and intermetallics), (3) spin-orbit coupling in 5*d*-states, magnetic dipole term, magneto-optical effect (M/Pt thin films and intermetallics), (4) indirect exchange (RKKY) interaction, onset of ferromagnetism (Heusler alloys and Pd disordered alloys). Exotic materials such as meteorite, biological substance, and organic materials are also attracting much interest. It is important to observe response in dichroic spectrum with external parameter, *e.g.*, high magnetic or electric field, high pressure, and high or low temperature.

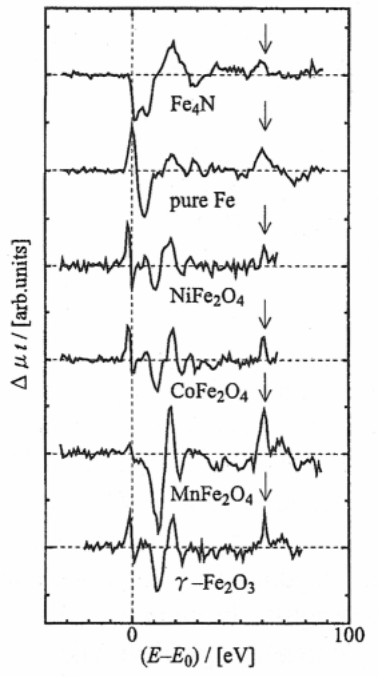

Fig.2 MEE in MCXD at Fe K-edge [6].

Dichroic signal in secondary process, occurring simultaneously with X-ray absorption, has been observable owing to advancement of SR and also is a powerful tool to probe electronic excitations.
Resonant Raman scattering [4], resonant X-ray emission spectrum [5], and multielectron excitation [6] (see Fig.2) are useful for comprehensive understanding of not only photoionization process but also electronic structure. Detection of fluorescent X-rays from a single crystal provides anisotropic information on the specified states.

3.1.2 X-ray magnetic diffraction (XMD)

X-ray magnetic diffraction is a technique to directly measure spin and orbital densities using the partially circular polarization. The cross section is described by spin S(*k*) and orbital L(*k*) parts of spatial Fourier transforms of angular momentum and degree of circular and linear polarization. When the polarization states are specified in advance, S(*k*) and L(*k*) can be uniquely determined from two equations resulting from the measurements in different geometry.
Magnetic form factor i s thus completely separated into S(*k*) and L(*k*) contributions, which is a notable , advantage differing from neutron diffraction. Feasibility of the measurement up to higher momentum transfer is significant.

From the viewpoint of anisotropy in magnetic form factor, the measurement of Fe and Co has been recently made by the white beam method in the range of k from 0.2 up to 2Å^{-1} on BL-3C1at KEK-PF [7]. From the result of the three principal axes of Fe, the observed profiles of (110) and (111) planes show zero-crossing at around k=0.8Å^{-1}, but the (100) profile always shows a positive sign, which are consistent with the data of neutron diffraction and band calculations. Anisotropic feature is more pronounced in the range of high-*k* from 1.2 to 2Å^{-1} rather than in low-*k* range. In the case of hcp-Co, however,

magnetic form factor of (100), (110) and (101) planes shows no anisotropic feature. This is a contrast with the results of Fe and indicates that strong crystalline magnetic anisotropy is not reflected in magnetic form factor.

It is very important to control the degree of polarization, so that we will apply the phase retarder system to the measurement by monochromatic beam method; that is, photon energy and polarization are tuned to suitable values for the 90° scattering. Furthermore, the switching of helicity allows us to apply high magnetic field to specimen by superconducting magnet. This can spread the research to hard magnetic materials too, *e.g.*, $R_2Fe_{14}B$ compounds.

3.2 Diffractometry using linear polarization

3.2.1 X-ray resonance magnetic scattering (XRMS)

Resonant scattering has contributed to discovery of new phenomena in diffractometry and to understanding of electronic structure since the pioneer work of Namikawa *et al*. [8]. X-ray resonance magnetic (exchange) scattering is still progressing in parallel with magnetic circular dichroism as a spectroscopy. In addition, this technique possesses the following unique characteristics differing from MCXD: (1) site-selectivity,(2)applicability to antiferromagnet, (3) resonant enhancement, (4) polarization dependence. Therefore, we will prefer magnetic structural study to dichroic spectroscopy in the initial stage. The vertical linear polarization, converted by the $\lambda/2$ phase plate, is suitable for this purpose in the intended geometrical configuration.

We have proposed magnetic scattering in manganese-fluoride antiferromagnet, e.g. , $RbMnF_3$, MnF_3, etc., on resonant condition at the Mn K-edge. Antiferromagnetic reflections will be studied in detail with temperature around the Néel point in connection with phase transition.

Intensity of the magnetic Bragg peaks is measured as a function of photon energy around the edge, and polarization analysis of the reflections is made to separate the a and π components.

Magnetite (Fe_3O_4) is a very interesting substance as a site-selective study by this technique. We will introduce magnetite for researching charge or spin ordering among Fe^{3+} and Fe^{2+} ions in polyhedral environment below the Verwey temperature. From the viewpoint of modulated magnetic structure, R-M thin-films and inter-metallic compounds also are attractive. In dichroic spectroscopy, separation of quadrupole component from dipole transitions has not reached general consensus yet. Effect of quadrupole transitions may appear the polarization states in a different way from the dipole transitions. To clarify the feature of photoabsorption excitation process, we will apply the polarization analysis to asymmetry ratio spectrum at R *L*-edge in $R_2Fe_{14}B$ system. The obtained knowledge will be useful for understanding of R 4f-electronic states and 4*f*-5*d* interaction.

3.2.2 X-ray magnetic Bragg scattering (non-resonant)

Polarization dependence of X-ray magnetic scattering cross section has been shown by Blume and Gibbs [1]. Since the matrix element includes spin $S(k)$ and orbital $L(k)$ densities, each component can be experimentally resolved through the polarization analysis of the scattered beam. It is difficult for neutron scattering to separate $S(k)$ and $L(k)$. Although this is one of the most attractive point of X-ray magnetic scattering, there is little experimental report up to the present.

For this experiment we prepare a single crystal of RIG(Rare-earth iron garnet: $R_3Fe_5O_{12}$), because (1) almost perfect crystal is obtainable, (2) Fe^{3+} ion has a large spin (S=5/2),(3) magnitude of S and L in R^{3+} ion varies with Hund rule. For the polarization analysis, multiple-beam diffraction technique [9] will be used as polarimetry to determine three Stokes-Poincaré parameters, which can be completely evaluated by doing three pairs of intensity measurements on a single Bragg reflection. The phase retarder can easily alter the π and σ polarizations of incident X-ray for the intended geometry. The obtained $S(k)$ and $L(k)$ profiles are compared with the results of X-ray magnetic diffraction.

Antiferromagnetic MnF_3 and $RbMnF_3$ also are interesting materials for this experiment.

4. International collaboration

The researches on magnetic property using SR have been developed into world-wide collaborations because of requirements of high-brilliance and qualified polarization in the 3rd generation facilities. We have made a research program at ESRF, collaborated with physicists of CNRS Grenoble in France, Zaragoza University in Spain, and INFN-LNF in Italy, for under-standing of spin-reorientation phenomena in the $R_2Fe_{14}B$ system [10]. As the outcome of the collaboration, Fig. 3 shows the asymmetry ratio spectrum at the Nd L_2-edge XRMS in $Nd_2Fe_{14}B$. This program will be made to develop into collaboration at SPring-8.

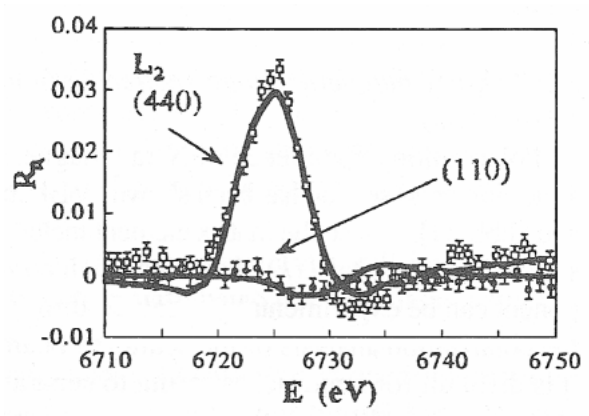

Fig.3 XRMS at Nd L3-edge in $Nd_2Fe_{14}B$. A comparison between experiment and calculation is shown.

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