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会合議事録

研究会名：物質における高エネルギーX線分光研究会

日　　　時：2012 年 8 月 25 日（土）　10：30-12：00

場　　　所：大阪大学吹田キャンパス R4 棟（材料開発・物性記念館）研修室

出席者：（議事録記載者に下線）

　　　　　　　福島整（物質・材料研究機構）、奥井真人（神津精機）、梅咲則正（高輝度光科学研究センター）、巽　修平（川崎重工業）、尾崎信司（パナソニック）、伊藤嘉昭（京都大学）、栃尾達紀（神戸大学）、本多信一（兵庫県立大学）、北川靖久（兵庫県立大学）

　　　　　　　<u>寺澤倫孝</u>（兵庫県立大学）

議題：

1）　　　研究会の経緯および状況報告（寺澤）

2）　　　活動状況及び国際共同研究プロジェクト（今年度開始）報告（伊藤）

3）　　　研究成果報告（福島）

議事内容：

1）本年4月より従来の SPring-8 利用者懇談会が SPring-8 ユーザー協同体（SPRUC）と改変され、参加する研究会を再編成する構想が通報さた。これに従い本研究会は設置をあらためて申請したところ承認された。これまでの活動の経緯を報告し、今後の活動の方針など、今年度より開始した国際共同研究 FP initiative Project（ 2)項参照 ）の推進についても議論した。

2）本研究会は 2012 年 4 月から開始される”Fundamental Parameter (FP) determination for improved XRF analysis and methodology development for reduced FP uncertainties”と題する国際共同研究プロジェクト（Project of FP initiative）に参加することになった。この開始にあたっては、契約書の作成・締結など準備会議を 2011 年 11 月から実施してきた。このプロジェクトはドイツ（物理工学連邦研究所）、スイス（フライブルグ大学）、フランス（サクレイ CEA－LNE/LNHB）、日本（京都大学化学研究所）の 4 研究機関がまとめ役となって進める 5 年～7 年間の計画である。質量吸収係数、遷移確率、コスタークローニッヒ遷移、発光スペクトルのエネルギー値、半値幅、蛍光収率、相対強度比、及び化合物の化学結合効果などの基本パラメーターの精度の向上など、蛍光 X 線に寄与するデータベースの改良を行い、産業利用に供するデータファイルを整備することを目標にして進める。これらのデータは古いものは数十年前に測

定されたものもあり、放射光施設が整備され X 線分光学の顕著な進展が見られるようになった現在、データの見直し、精度向上が必要になっている。日本では京大化研の伊藤グループが中心となり、とくに SPring-8 を利用して BL14B2 に設置した高分解能２結晶分光器による測定がこのプロジェクトに大きく寄与することが期待されている。SPring-8 が最先端高性能放射光源の施設としてその期待は大きい。

３）蛍光 X 線に代表される原子からの発光 X 線スペクトルを中心として
基礎から応用及び計測系を包括する代表的な国際会議（２年に１回開催）の"The 14th European Conference on X-Ray Spectrometry (EXRS 2012) " がウィーンで開催された。参加して本研究会から下記４件の研究発表を行った。すべて SPring-8／BL14B2 を利用し、２結晶発光分光スペクトロスコピーを行った研究成果である。

i)   Probing the Ba 5d states in BaTiO3 and BaSO4: A resonant x-ray emission study at the Ba-L3 edge; K. Yoshii *et al*.

ii)   Determination of Co and Fe *K* absorption edge using the high-resolution X-ray fluorescence emission spectra; Y.Ito *et al*.

iii)   The Observation of The Profile Change of Fe $K\alpha 1, 2$ spectra using excitation energy around *K*-absorption Edge; S. Fukushima *et al*.

iv)   Quantitative Determination of the Oxidation state of Fe in Fe3O4 by High-resolution X-ray Fluorescence Spectroscopy; S. Fukushima *et al*.

各論文のアブストラクトを別途資料として添付する。

Quantitative Determination of the Oxidation state of Fe in Fe₃O₄ by High-resolution X-ray Fluorescence Spectroscopy

S. Fukushima[1], Y. Ito[2], T. Fujii[3], T. Tochio[4], M. Terasawa[5], K. Yoshii[6]

and Y. Yoneda[6]

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The oxidation state analysis of Fe in several kinds of compounds or materials has strongly been requested, because this information is so important to reveal the expression mechanism of the property of Fe contained materials. In addition, any technique for this aim should be non-destructive in practical. On the basis of this point, this group has been investigated for the application of the combination of High-Resolution X-ray Fluorescence Spectroscopy (HRXRF) and non-linear least square curve fitting analysis using measured spectra [1] as the component profiles. The x-ray spectral measurement was executed for using RIGAKU 3570EKI system. This system had the double-crystal monocromator with (+, +) setting [2,3], and two Si(220) crystals were used as analyzer.

High-resolution Fe $K\alpha_{1,2}$ spectrum of Fe_3O_4 and the result of the curve fitting analysis are shown in Fig.1. The result of the analysis shows that about 90% of Fe in Fe_3O_4 should be Fe^{3+}. The similar result was obtained from the experiment using the same type spectrometer in the SPring-8 BL14B1. In contrast, the case using Fe $K\beta$ was shown in Fig.2, and the result of the analysis show the reasonable conclusion as $Fe^{2+}:Fe^{3+} = 1:2$. Thus, it can be concluded that using Fe $K\beta$ is suitable for the quantitative oxidation state analysis in practical. The result of the oxidation analysis of Fe in $RuFeO_3$ will also be presented in the poster. The difference between $K\alpha_{1,2}$ and $K\beta_{1,3}$ spectra has been investigated on the basis of the considerations.
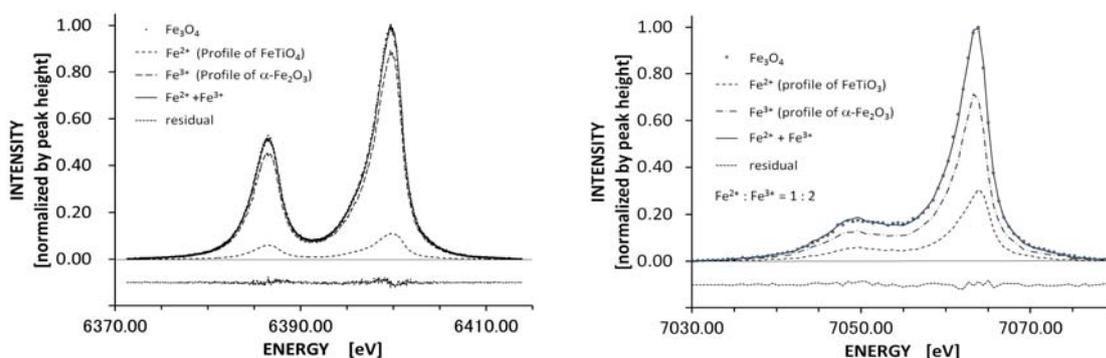
Fig.1 The result of the analysis using Fe $K\alpha$.   Fig.2 The result of the analysis using Fe $K\beta$.

[1] S.Fukushima, T.Maruyama, K.Yamada and E.Takahashi, Advances in X-ray chemical analysis, Japan, Vol.25 (1994) 79-91.
[2] Y.Gohshi, H.Kamada, K.Kohra, T.Utaka and T.Arai, Applied Spectroscopy 36 (2) 1982, 171-174.
[3] T. Tochio, Y. Ito, and K. Omote, Phys. Rev. A65 2002, 042502-1~6

The Observation of The Profile Change of Fe $K\alpha_{1,2}$ spectra using excitation energy around K-absorption Edge

S. Fukushima[1], K. Uchida[2], Y. Ito[2], M. Huruya[3], T. Fujii[3], T. Tochio[4],

M. Sato[5], T. Ninomiya[5] and M. Terasawa[6]

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When the oxidation state analysis of Fe using high-resolution X-ray florescence spectroscopy is carried out, it has often been observed that Fe^{2+} state is almost covered by Fe^{3+} state using W or Rh target, sufficiently higher excitation energy than Fe K-absorption edge. One of the typical examples is the case of Fe_3O_4. For investigation about this phenomenon by means of RIXS, the observation of the spectral change of Fe $K\alpha_{1,2}$ emission lines was executed for in the Fe oxides changing the excitation energy around Fe K threshold.

The high-resolution Fe $K\alpha$ measurement was executed using RIGAKU 3570EMF system in BL46XU in SPring-8, which had the double-crystal type monchromator [1,2] with two Ge(111) crystals.

Fig.1 shows the measurement result of Fe $K\alpha_{1,2}$ spectra in Fe_3O_4 with the excitation energies. All the spectra shown in this figure were analyzed with non-linear least square curve fitting method with measured spectra as the component profiles [3] for the decision of the existence ratio between Fe^{2+} and Fe^{3+}. The result of the analysis and the changes of the peak top intensity
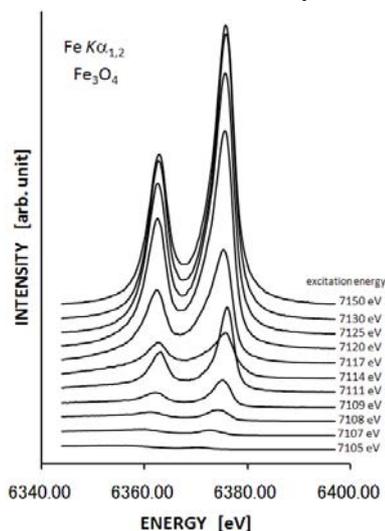
Fig.1   The profile change of Fe $K\alpha_{1,2}$ spectra with the excitation energy.
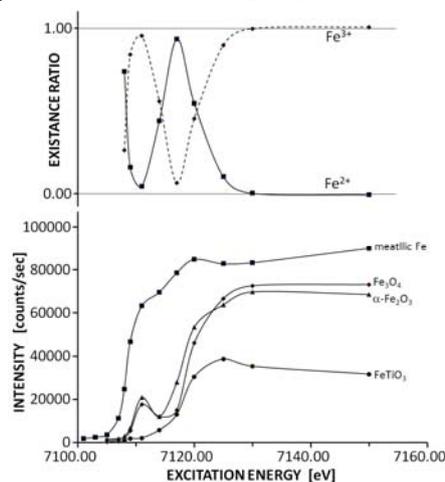
Fig.2 The change of Fe $K\alpha$ peak top intensuty, and the result of the curve fitting for Fe_3O_4 tin proportion to the excitation energy.

of Fe Kα in proportion to the excitation energy was shown in Fig.2. It is so interesting that the spectrum of Fe_3O_4 excited with 7117eV shows the almost same profile of $FeTiO_3$ (Fe^{2+}). And, the investigation about this phenomenon has been discussed at present.

[1] Y.Gohshi, H.Kamada, K.Kohra, T.Utaka nad T.Arai, Applied Spectroscopy 36 (2) 1982, 171-174.
[2] T. Tochio, Y. Ito, and K. Omote, Phys. Rev. A65 2002, 042502-1~6.
[3] S.Fukushima, T.Maruyama, K.Yamada and E.Takahashi, Advances in X-ray chemical analysis, Japan, Vol.25 (1994) 79-91.

Determination of Co and Fe *K* absorption edge using the high-resolution X-ray fluorescence emission spectra

Y.Ito[1], N.Shigeoka[1], H.Ohashi[1], T.Tochio[2], S.Fukushima[3], M.Terasawa[4],

T.Fujii[5], H.Kageyama[6], K.Yoshii[7], Y.Yoneda[7] and A.Nisawa[8]

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For the fluorescent X-ray spectra excited with the energy near or around the absorption edge, the spectral change generally appears in the profile. One of the important phenomena under such excitation condition is the process that an inner shell electron is excited to any unoccupied orbital just below the valence band (resonance excitation) and the subsequent electron transition from an occupied orbital to inner shell is caused (RIXS). On the other hand, in the case that no resonance excitation occurs in the atom, the spectral change can be also observed in the excitation energy region just below the absorption edge (electron Raman scattering). This kind of change can be interpreted to the excitation of inner shell electron to the virtual level that is described as the partially unoccupied level. Thus, the emission spectrum profile appears in the form that is missing in the high energy side of the spectral profile in the fluorescence region. When the excitation energy goes just under the threshold for the ejection of the electron to the vacuum level, the profile and peak position of the x-ray spectrum begin to change. It is considerable that the point between the fluorescent X-ray region and electron Raman scattering region should correspond to the X-ray absorption edge, and this fact gives the practical and physical method to decide the energy value of absorption edge clearer than the direct measurement of the absorption edge.

The experiments were executed for the X-ray emission spectra in Fe and Co, respectively at SPring-8 BL14B1. The high resolution X-ray fluorescent spectra were measured using a RIGAKU system 3570EMF with double-crystal type spectromator [1, 2].

The result of the measurement of Co $K\alpha_{1,2}$ of metallic Co is shown in Fig.1, for example. $K\alpha_{1,2}$ spectra show the clear edge at 7707.2eV. The energy position of this value can be defined as the absorption energy value of metallic Co K-edge.
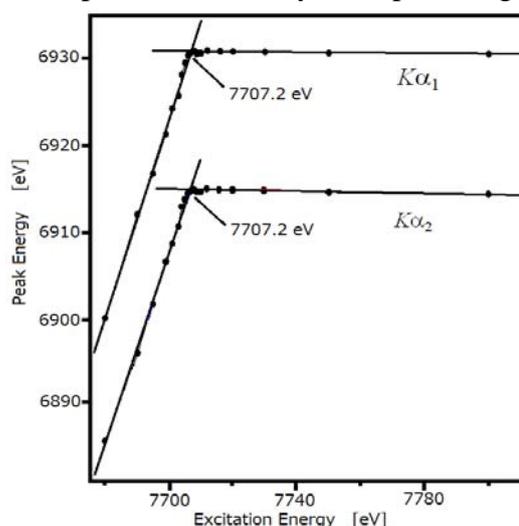
Fig.1   The changes of the peak positions of Co $K\alpha_{1,2}$ spectra in metallic Co.

[1] Y. Gohshi, H. Kamada, K. Kohra, T. Utaka and T. Arai, Applied Spectroscopy 36 (2) (1982) 171-174.
[2] T. Tochio, Y. Ito, and K. Omote, Phys. Rev. A65 (2002) 042502-1~6

Probing the Ba 5d states in $BaTiO_3$ and $BaSO_4$: A resonant x-ray emission study at the Ba-L_3 edge

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We have directly probed the Ba 5d states in the ferroelectric barium titanate $BaTiO_3$ using two bulk-sensitive spectroscopic probes, resonant x-ray emission spectroscopy (RXES) and x-ray absorption spectroscopy in the partial fluorescence mode (PFY-XAS) at the Ba-L_3 edge. The results are compared with those of the non-ferroelectric barium sulfate $BaSO_4$.

The experiments were carried out using synchrotron radiation at the BL-15XU beamline of SPring-8 [1]. It was found that while the RXES spectra point to a localized character for the Ba 5d states in both compounds, the main peak of the PFY-XAS spectrum, corresponding to the dipolar transitions from 2p to 5d, is found to be significantly broader for $BaTiO_3$ than for $BaSO_4$. On the basis of band structure calculations, this broadening is ascribed to strong hybridization between the unoccupied Ba 5d and O 2p states in the ferroelectric phase. This suggests that the hybridization between the conduction states of the Ba^{2+} and O^{2-} ions, and not only Ti^{4+} and O^{2-}, plays a central role in determining the electronic structure of $BaTiO_3$, and is therefore likely to be indirectly correlated with the occurrence of ferroelectricity in this material.

[1] D. Horiguchi, K. Yokoi, H. Mizota, S. Sakakura, H. Oohashi, Y. Ito, T. Tochio, A. M. Vlaicu, H. Yoshikawa, S. Fukushima, H. Yamaoka and T. Shoji, Rad. Phys. Chem. **75** (2006) 1830-1834.