

## Chapter II: Review of Literatures

Qxgt "y j g" { gctu'pwo gtqwu'y qtmu'j cxg'dggp'f qpg'qp "V<sub>4</sub>Q" dcugf "o cvgtknu" kp'xlgy "qh'ku'xctkqwu" vgej pqm<sub>i</sub> kcn'cpf "cr r rkecvkp" cur gewu'Vj ku'ej cr vgt 'f gcu' y kj " y j g" rkygtcwtgu" tgrvgtf " vq" o ci pgve. " tcur qt v' cpf " kqp" ktcf kcvkp" dcugf " uwf lgu" qp "V<sub>4</sub>Q" cpf " tcurvkvkp" o gcn'f qr gf "V<sub>4</sub>Q'Vj g" tgrxcpv' tguwu" qp " y j g" o ci pgve" cpf " tcur qt v' r tqr gt vku" qh'V<sub>4</sub>Q" cu' y gm' cu' tcurvkvkp" o gcn'f qr gf " V<sub>4</sub>Q" ctg' f kuewu'gf " kp" Ugevkqp" 4B" cpf " Ugevkqp" 40 " tgr gevkxgn' (0'Ghgewu" qh' kqp" ko r rcpvkvkp lktcf kcvkp" qp" utwewt'cn' cpf " o ci pgve" r tqr gt vku" ctg' f gr kvgf " kp" Ugevkqp" 450' Vj g' f kuetgr cpeku" kp" y j g" qdugt xgf " o ci pgkuo " kp" y j g" qz kf g" u{ uvo u' ctg' f kuewu'gf " kp" ugevkqp" 460' Vj g" qdlgevkgu" qh' y j g" r tgu'gpv' y j g" u' ctg' qwv'kp'gf " kp" Ugevkqp" 470

### 2.1 Magnetic Properties

Vj ku'ugevkqp' f gcu' y kj " y j g" o ci pgve" r tqr gt vku" tgr qt vgtf " kp" V<sub>4</sub>Q" cu' y gm' cu' tcurvkvkp" o gcn' f qr gf " V<sub>4</sub>Q' Ugevkqp" 48B" i kxgu" c" dtlgh" f gwckl' qh' y j g" qdugt xgf " hgttqo ci pgkuo " kp" V<sub>4</sub>Q" y j gtgcu" Ugevkqp" 404 " uwo o ctkgu" y j g" qdugt xgf " hgttqo ci pgkuo " kp" xctkqwu' tcurvkvkp" o gcu' rkn'g " Eq. " Hg. " Et. " X. " Ew. " P k' Cn' P d' cpf " O p' f qr gf " V<sub>4</sub>Q

#### 2.1.1 Magnetism in TiO<sub>2</sub>

Tqqo " vgo r gtcwtg" hgttqo ci pgkuo " \*TVHO + " kp" V<sub>4</sub>Q" y cu' hku'v' tgr qt vgtf " d { " J qpi " gv'cn'0\*4228 + 'cpf " [ qqp " gv'cn'0\*4228 + " kp" y j kp' hku' u' f gr qukvgtf " qp " NcCrQ<sub>5</sub>" uwdutcvg" y j gtg' y j g" V<sub>e</sub> y cu' hct " dg { qpf " y j g' tqqo " vgo r gtcwtg' Hwtv j gt. " y qtm' kp" V<sub>4</sub>Q" y cu' hqmny gf " d { " Twco ck " gv'cn'0\*4229 + " cpf " Mko " gv'cn'0\*422; + " y j gtg' y j g" qdugt xgf " hgttqo ci pgkuo " y cu' uqngn' " cuetkdgf " vq" qz { i gp" xcepeku' Vj ggtgkcm { . " Rgpi " gv'cn'0\*422; + " uwi i guvgf " y j g' hqto cvkp " V<sub>k</sub> xcepe { " vq" ecwug" hgttqo ci pgkuo " kp" V<sub>4</sub>Q' Vj g' V<sub>k</sub> xcepeku' ctg' cdng' vq' r tqf weg' c' pgv' o ci pgve" o qo gpv'  $\epsilon 507 \mu_B$  " r gt" xcepe { " y j gtgcu" V<sub>k</sub> f kxcepku' cnuq" r tqf weg" pgv' o ci pgve" o qo gpw' qh' y j g' o ci pkwf g'  $\epsilon 407 \mu_B$  " r gt" f kxceppe { 0' Y j gp' y j g' y q" V<sub>k</sub> xcepeku' ugewt g' y j g' pgctgu' ukgu. " cp " Q<sub>4</sub> f ko gt " ku' uwr r qugf " vq" hqto " cv' y j g" egpvt' qh' y j g' f kxceppe { " y j cv'ngcf u' vq" c' f getgcug' kp' y j g' vcn' gpgti { " cu' y gm' cu' kp" o ci pgve" o qo gpv' 0' Gpgti gkcm { . " gkj gt " V<sub>k</sub> xcepeku' qt " f kxcepku' hcqw' y j g" hgttqo ci pgve" qtf gt " y j qwi j " k' j cu' pqv' guxcdruj gf " gzt rtko gpvcn' { 0' [ qqp " gv'cn'0

\*4228+"uj qy gf "V<sub>E</sub>"v"dg"ctqwpf ": : 2"M'hqt"cpvcug"V<sub>kQ</sub><sub>4</sub>"hko "qp"NcCr<sub>Q</sub><sub>5</sub>"\*322+"  
 uwdutcvg"wukpi "RNF"vgej pls wg"cpf "gZR mcpkf "vj g"o ci pgvkuo "qp"vj g"dcuku"qh"  
 f qwdng"gzej cpi g"o gej cpluo "] [ qqp"gv'cr0'\*4228+\_0O kZgf "r j cug"qh'cpvcug"cpf "  
 twkng'hko u'i tqy p"qp"Uk'cpf "s wctv "uwdutcvg"uj qy kpi "hgttqo ci pgvkuo "j cu'dggp"  
 cuetkdgf "v"etgcvkp"qh"qz { i gp"xcecpelgu"vj cv'ngcf u"v"Uqpgt"ur rkwkpi "qh'dcpf u"  
 ecwukpi " vj g" hgttqo ci pgvk " qtf gtlpi " ]T wo ck " gv' cr0' \*4229+\_0' Vj g" ghgev' qh"  
 cppgcrkpi " qh' V<sub>kQ</sub><sub>4</sub>" hko u" y cu" hqwpf " v" f getgcug" vj g" o ci pgvk " o qo gpv' cpf "  
 tgf wvki " vj g" vj kempgu" j cu" uj qy p" v" gpj cpeg" vj g" uco g" kp" V<sub>kQ</sub><sub>4</sub>" twkng" hko u"  
 f gr qukvf " d { " ur kp" eqcvki " cpf " ur wwt " f gr qukvkq " vgej pls wgu" qp" s wctv " cpf "  
 ucr r j k g" uwdutcvg. " t gur gev x gn [ ] Uwf cnet " gv' cr0' \*422: +\_0' Hgttqo ci pgvkuo " y cu"  
 vki i gtgf " d { " vj g" hqt c vkp " qh' V<sub>k</sub><sup>5</sup> / X<sub>Q</sub> " f ghgev' eqo r ngz " cu' tgr qtvgf " d { " Z kpi " gv"  
 cr0' \*4235+" kp" twkng" V<sub>kQ</sub><sub>4</sub>" ukpi ng' et { ucu" wpf gt " xcewwo " cppgcrkpi " ] F qpi / Z kpi "  
 gv' cr0' \*4235+\_0' Vj g" ghgev' qh' cpvcug" cpf " twkng" r j cug" qp" o ci pgvk " r tqr gt vku" qh"  
 V<sub>kQ</sub><sub>4</sub>" hko " f gr qukvf " d { " uqn' i gn' ur kp" eqcvki " o gvj qf " qp" C<sub>n</sub>Q<sub>5</sub>" \*2223+" y cu"  
 uwf kfg " d { " Mko " gv' cr0' \*422; +\_0' Vj g { " j cxg" uj qy p" vj cv' V<sub>kQ</sub><sub>4</sub>" kp" cpvcug" j cu" nqy gt "  
 o ci pgvk " o qo gpv' vj cp" kp" twkng" r j cug' V<sub>kQ</sub><sub>4</sub>" pcpqr ct vengu" u { pvj guk gf " d { " uqn'  
 i gn' tqwg" uj qy gf " j ki j gt " o ci pgvk " o qo gpv' wpf gt " cti qp" cppgcrkpi " ] I j quj " gv' cr0'  
 \*4235+\_0' Twkng" V<sub>kQ</sub><sub>4</sub>" pcpqy ktgu" i tqy p" qp" Uk" \*223+" cpf " i nuu" uwdutcvgu" wukpi "  
 uqrxqj gto cn' vgej pls wg" ctg" uj qy p" v" j cxg" j ki j gt " ucwcvkq " o ci pgvkucvkp " \*O<sub>u</sub>+"  
 kp" eqo r ctluqp " v" P K' f qr gf " V<sub>kQ</sub><sub>4</sub>" kpf kecvki " o ci pgvkuo " qtki kpcvki " htqo " vj g"  
 uwthceg" f ghgeu" rknng" V<sub>k</sub><sup>5</sup> " cpf " qz { i gp" xcecpelgu" ] J qc" gv' cr0' \*4235+\_0' kp" ecug" qh"  
 twkng" V<sub>kQ</sub><sub>4</sub>" pcpqr ct vengu" u { pvj guk gf " d { " ej go kecn' j { f tqn' uku" o gvj qf . " t g x g c r g f "  
 o ci pgvkuo " qtki kpcvki " htqo " qz { i gp" xcecpelgu" ] Rcttcu" gv' cr0' \*4235+\_0' V<sub>kQ</sub><sub>4</sub>"  
 r gmgv" qh' twkng" wr qp" ko r mpcvkq " qh' 6" O gX" Ct<sup>7</sup> " kq " f go qpucvfg "  
 hgttqo ci pgvkuo " cv' tqo " vgo r gtcwtg" ] Ucp { cr' gv' cr0' \*4236+\_0' " Ucpvctc" gv' cr0'  
 uj qy gf " qz { i gp" xcecpelgu" " o gf kvgf " hgttqo ci pgvkuo " kp" V<sub>kQ</sub><sub>4</sub>" pcpqt kddapu"  
 ] Ucpvctc" gv' cr0' \*4236+\_0' Tgegpv. " wukpi " hktuv' r tkpek ngu" ecwvkvapu. " vj g"  
 eqgz kvpeg" qh' V<sub>k</sub>' xcecpelgu" cpf " Q' xcecpelgu" ctg" hqwpf " v" dg' t gur qpukdnng' hqt " vj g"  
 qdugt xgf " hgttqo ci pgvkuo 0' Ecwvkvapu" j cxg" uj qy p" vj cv' qz { i gp" xcecpelgu" { " ecp"  
 kpf weg" mcecn' o ci pgvk " o qo gpv' kp" V<sub>kQ</sub><sub>4</sub>. " j qy gxgt. " vj g" hgttqo ci pgvk " gzej cpi g"  
 kvgtcevkvq " qh' y q' xcecpelgu" ku" pqv' utqpi " gpqwi j " v" kpf weg" tqo / vgo r gtcwtg "

hgttqo ci pgvkuo "qp" vj gkt "qy p" kp" VkQ4' Vj g" HO " eqwr rkp " dgwy ggp" y q" Vk' xcecpelgu'ku'cdqwf'hqwt'ko gu'utqpi gt'vj cp'vj cv'dgwy ggp'y q'qz {i gp'xcecpelgu' y j lej 'ku'hqwpf "vq'dg'gpj cpegf "y kj "vj g'r tgugpeg"qh'qz {i gp'xcecpe {0Dcukem{ . " vj g" grgextqpu" kpf wegf " d{ " qz {i gp" xcecpelgu'o gf kvg" vj g" mpi /tcpi g" hgttqo ci pgvke "gzej cpi g"kpvtcevkqp "dgwy ggp"y q" f kvcpv'Vk'xcecpelgu"Y cpi "gv' crf' \*4236+\_0' [ cpi " gv' crf' \*4232+" uj qy gf " vj gqtgvkcm{ . " vj cv' c" mecn' o ci pgvke" o qo gpv' qh'3QÜb"r gt" Vk<sup>5</sup> "kp" vj g" rkwleg0' Vj g"ecrwwcvgf "tguwmu"ctg"kp" i qqf " ci tggo gpv'y kj "vj g"gzr gtko gpvcn{ "qdugt xgf "cpvkhgttqo ci pgvke "rkg"dgj cxlqt"kp" qz {i gp/f ghlekpv'Vk/Q"u{ uvgo u0'Vj g"gzegu"grgextqpu"kpvtqf wegf "d{ "cp"qz {i gp' xcecpelgu' { "eqpxgtv'y q"Vk<sup>6</sup> "kpu"kpq"y q"Vk<sup>5</sup> "kpu"cpf "tguwmu"kp" c"mecn' o ci pgvke" o qo gpv' kp" cpcvug" r j cug0' J qy gxgt. " vj g" y q" Vk<sup>5</sup> " kpu" hqto " c" ucdrg" cpvkhgttqo ci pgvke "ucvgo'Vj g"v gpf "ku'uko krc "hqt"qz {i gp/f ghlekpv'twkngr" j cug" VkQ4' Vj g"ecrwwcvgf "tguwmu"ctg"eqpukv'v'y kj "vj g"gzr gtko gpvcn{ "qdugt xgf " cpvkhgttqo ci pgvke" dgj cxlqt" kp" qz {i gp/f ghlekpv' Vk/Q" u{ uvgo " ] [ cpi " gv' crf' \*4232+\_0'

P qv'qpn{ "kp"VkQ4. "Uwpcf tgucep"gv'crf' \*4228+"tgr qtvgf "vj g" hgttqo ci pgvkuo " cu" c" wpxgtucn' hgcwtg" qh' pcpqr ctveng" qh' kpqti cple" qz kf gu' f wg" vq" gpj cpegf " uwthceg" f ghgeu' rkg" qz {i gp' xcecpelgu' Uko krc "wpgzr gevfg " hgttqo ci pgvkuo "y cu" cnuq' tgr qtvgf "kp" J hQ4' vj kp' hko u'd { 'Eqg{ "gv'crf' \*4227+" y j lej "hwt vj gt' utgpi vj gpu" vj g" f ghgev' kpf wegf " o ci pgvkuo "kp" vj gug" u{ uvgo u0' Vq" gzr rkp" vj g" o ci pgvkuo "kp" vcpukvqp" o gvcn' f qr gf "VkQ4. " vj gtg" ctg" ugxgtcn' o qf gnu" r tqr qugf "kp" rkgtcwtg" uwej " cu" Twf gto cp/Mkwgn/Mcuw{ c/[ qukf c" \*TMM [ +" o qf gn" Dqwpf " O ci pgvke" Rqrctqp" \*DO R+" o qf gn" cpf " Uqpgt" v{ r g" o qf gn' cu" f kuewugf " kp" Ej cr vt " K' J qy gxgt. "vkn'pq'ukpi ng" o gej cpluo "eqwf "gzr rkp" vj g" qdugt xgf " hgttqo ci pgvkuo " kp" vj gug" wpf qr gf " qz kf g" u{ uvgo u" ucvkucvqt kn' 0' O qtgqxt. " vj g" o quv' eqo o qp" hgcwtg' kp' cm' vj gug" o gej cpluo u'ku' vj g' xkcn' tqrng' r r { gf " d{ " vj g" kpvtcevkqp" co qpi " vj g" ej cti g" ecttkgtu" cpf " vj g" o ci pgvke" o qo gpv" vj cv' f gekukxgn{ " eqpvtqn' vj g" grgextke" cu' y gni' cu' o ci pgvke" qtf gtlpi "kp" vj gug" qz kf g" o cvgtkcn0"

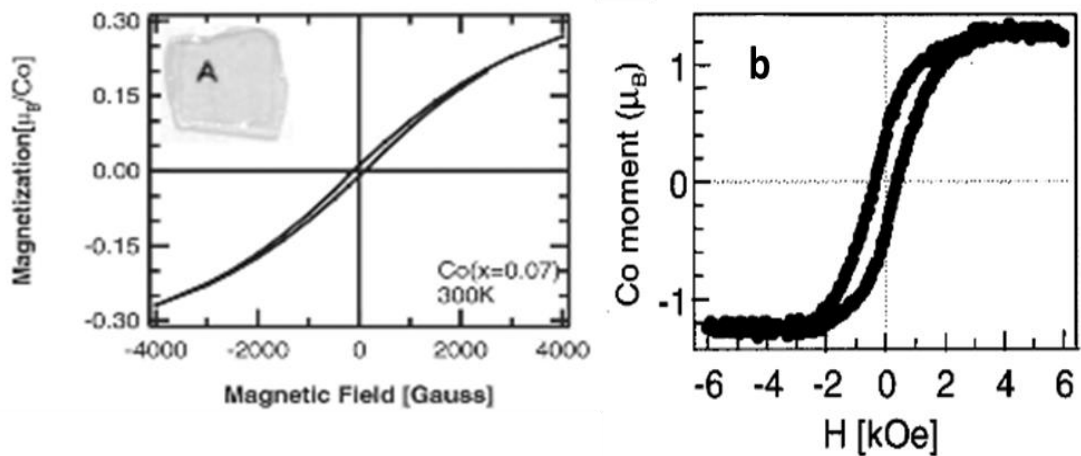
Vj g' hgttqo ci pgvkuo "ku' eqpukf gtgf "vq" gpj cpeg" kp" ecug" qh' vcpukvqp" o gvcn' f qr kpi "kp" VkQ4' j quv' Vj g' pgzv' ugev' kpf " f gvcn' y kj " vj g" xctkqwu' vcpukvqp" o gvcn' f qr kpi "kp" VkQ4' u{ uvgo u' cu' tgr qtvgf "kp" rkgtcwtgu0'

### 2.1.2 Magnetism in Transition Metal Doped TiO<sub>2</sub>

Vj ku'ugevqp"tgxky u"vj g"fhgtgpvtgr qtw"cxckrdng"qp"tcpuvklqp"o gcn' \*gđ 0'Eq.'Hg.'O p.'Et.'P k'Ew.'P d.'cpf "X+f qr gf "V<sub>2</sub>O<sub>4</sub>'

#### Co-doped TiO<sub>2</sub>

Y g"j cxg"fkuewugf "j gtg"vj g"uwf kgu"qp"Eq/f qr gf "V<sub>2</sub>O<sub>4</sub>"F O U"o cvgtkcn'kp" c"ej tqpmqj kcn'o cpgt0'O cuwo qv"gv'crđ\*4223+"j cf "tgr qtvf "hgttqo ci pgvuo " kp"Eq/f qr gf "cpcvug"V<sub>2</sub>O<sub>4</sub>"vj kp"hm u"i tqy p"d {"c"eqo dkpcvtkcn'r wugf "rcugt" f gr qukvqp" \*RNF+" cpf " o qrgewrt" dgco " gr kcz {" \*O DG+" vgej pls wg" y j lej " gpj cpegf "vj g'hgttqo ci pgv"qtf gt"vr vq"622"m"j cxkpi "o ci pgv"o qo gpv'qh"2054" D IEq"ht"9"cvđ "Eq"\*Hk 0'4B\*c+."r tkqt"v"vj g"fkueqxt {"qh'hgttqo ci pgvuo "kp" Op"f qr gf "\ pQ" ]Uj cto c" gv'crđ\*4225+\_0'Uqqp" chgt."Ej co dgtu"gv'crđ\*4223+" uj qy gf "vj g"gpj cpegf "hgttqo ci pgv"o qo gpv'vr vq"3048" D IEq"kp"qz {i gp'r rno c" cukvvgf "\*QRC+"O DG"hm "y kj "tgr vkgf {"mgy gt"Eq"eqpegpvcvqp"\*Eqđ5"cv' + \*Hk 0'4B\*d+" ]Ej co dgtu"gv'crđ\*4223+\_0'



**Fig.2.1** O ci pgvkvqp" cu" c" hwpevqp" qh" cr rkgf " o ci pgv" hgrf " hqt" \*c+ V<sub>2</sub>O<sub>5</sub>Eq<sub>209</sub>Q<sub>4</sub>/ "hm " cpf " ]O cuwo cv" gv' crđ\*4223+\_ "d+ V<sub>2</sub>O<sub>9</sub>Eq<sub>205</sub>Q<sub>4</sub>/ "hm " ]Chgt"Ej co dgtu"gv'crđ\*4223+\_

Vj g"hm u"uj qy gf "hgttqo ci pgvuo "y gtg"qh"cpvcug"r j cug"qpn(0'Chgt"qpg" {gct."Rctm"gv'crđ\*4224+"f go qputcvf "hgttqo ci pgvuo "kp"Eq/f qr gf "twkrg"hm u" f gr qukvf "d {"ur wwtkpi "vgej pls wg"y kj "gpj cpekp "vj g"V<sub>E</sub>"dg {qpf "622"m"vj g" o ci pgv"o qo gpv'y cu"20 6" D IEq"ht"Eq"eqpegpvcvqp"đ8"cvđ "y j lej "y cu" ngu"vj cp"vj g"o qo gpv'tgr qtvf "kp"cpvcug"r j cug" ]Rctm"gv'crđ\*4224+\_0'Uj ko "gv'crđ

\*4224+"qdugtxgf "f getgcug"kp"o ci pgvkucvkqp"htqo ": 7"go wlee"vq"54"go wlee"y kj " kpetgcukpi "Eq"eqpepvtcvkqp"htqo "3"vq"; cv " ]Uj ko "gv'crf0\*4224+\_0Ncvgt."Mko "gv' crf0'hqwpf "c"xctkcvkqp"kp"o ci pgvk"o qo gpv'htqo "207"vq"4047" D" hqt"6"cv "Eq/ f qr gf "cpcvcug"VkQ4"hkro u'f gr qukvgf "qp"Ut VkQ5"\*223+"uwdutcvgu"d {"kpetgcukpi " vj g" qz {i gp" r ctvken" r tguuwtg" htqo " 3z32<sup>9</sup>" vq" 3z32<sup>6</sup>" Vqtt" go r rj {kpi " " RNF " vgej pls wg"]Mko "gv'crf0\*4224+\_0C"tgrvkvgn{ "j ki j "o ci pgvk"o qo gpv'qh'60" D"y cu" qdugtxgf "d {"O cpkxcpcp"gv'crf0\*4225+"kp"j {f tqi gpcvfg "cpcvcug"Eq/f qr gf "VkQ4" pcpqr ctvkgu"y kj qw'cp {"uki pcwtg"qh"Eq"enwvgtkpi 0Mko "gv'crf0\*4225+"tgr qt vgf " o ci pgvk" o qo gpv' qh' 3077" D" kp" cpcvcug" Eq/f qr gf " VkQ4" \*9" cv0 +" hkro u' f gr qukvgf "d {"rcugt" o qrgewrt "dgco " gr kcz {" qp"NcCrQ5"uwdutcvg0'Uko kret"vq" Rctm'gv'crf0\*4224+"Uco r g"gv'crf0\*4225+"cnuq"qdugtxgf "vj g"o ci pgvk"o qo gpv'vq" dg"0"30" D"kp"ecug"qh"cpvcug"hkro "f gr qukvgf "qp"NcCrQ5"uwdutcvg"y j kej "y cu" j ki j gt"vj cp"vj g"qdugtxgf "208 D" hqt"twkrg"hkro "f gr qukvgf "qp"CnQ5"uwdutcvg0' Uj kpf g"gv'crf0\*4225+"f go qputcvfg "hgttqo ci pgvkuo "kp"9"cv0 "Eq/f qr gf "cpcvcug" hkro "f gr qukvgf "qp"Ut VkQ5" \*223+" uwdutcvg" y kj "c" o ci pgvk" o qo gpv' 306" D" rjy gt"vj cp"vj cv'qh"hkro "f gr qukvgf "qp"NcCrQ5"uwdutcvg" ]Mko "gv' crf0\*4225+\_0' Wukpi " c" ur tc {" r {tqn{uku" vgej pls wg." O cpkxcpcp" gv' crf0' \*4225+" qdvcvkgf " c" o ci pgvk"o qo gpv'qh"5" D" hqt"32"cv "Eq/f qr gf "cpcvcug"hkro u'i tqy p"qp"i rnuu" uwdutcvg"y j kej "ku's vkg"j ki j 0'Enwvgtkpi "qh"Eq"y cu"qdugtxgf "kp"Eq"ko r rcpvfg " VkQ4"hkro u'i kxkpi "tkug"vq" hgttqo ci pgvk" qtf gt"kp"hkro u'f gr qukvgf "qp" Ut VkQ5" uwdutcvg" y kj "c" o ci pgvk" o qo gpv' 030" D" ]Mko " gv' crf0' \*4225+\_0' Uko kret" enwvgtkpi "qh"Eq"y cu"tgr qt vgf "d {"Mgppgf {"cpf "Uco r g"\*4225+"y kj "xct {kpi "Eq" htqo "2027"vq"506"cv0 0J qpi "gv'crf0\*4226+"qdugtxgf "hgttqo ci pgvkuo "kp"34"cv0 " Eq/f qr gf "VkQ4"hkro u'f gr qukvgf "qp"NcCrQ5"uwdutcvg"]J qpi "gv'crf0\*4226+\_0'P q" ej cpi g"kp"ucwvkvkqp"o ci pgvkucvkqp"kp"ecug"qh"cpvcug"Eq/f qr gf "VkQ4"\*207" D+" pcpqr ctvkgu"y kj "z"? "207"cpf "208"y cu"qdugtxgf "d {"Ej q"gv'crf0\*4226+\_0C"j ki j gt" o ci pgvk"o qo gpv'\*604" D+"enqugt"vq"vj g'dwmiEq"kp"j ki j "ur kp"ucvgy"y cu'cej kxgf " d {"Dt {cp"gv'crf0]Dt {cp"gv'crf0\*4226+\_0"

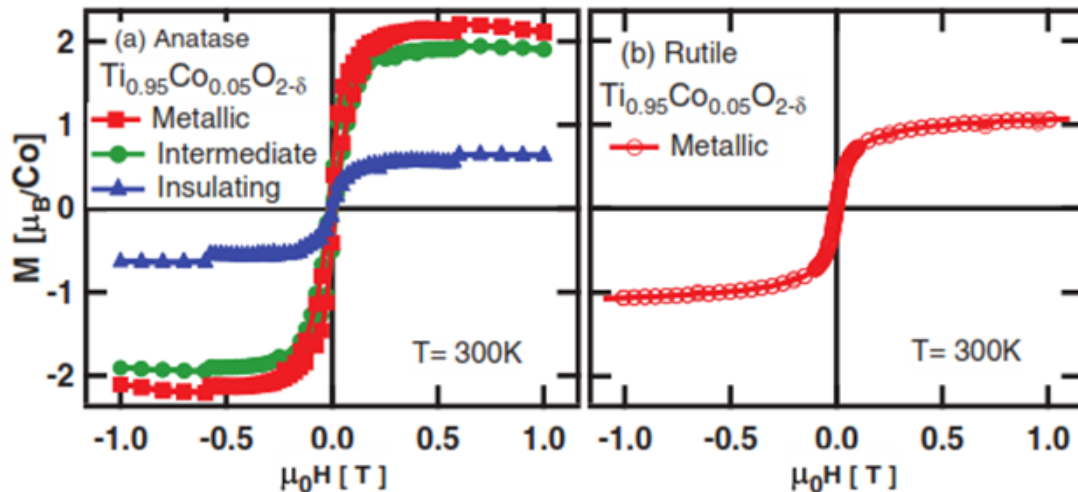
Uj kpf g"gv'crf0\*4226+"pqvkegf "vj g"o ci pgvk"o qo gpv'04" D"kp"twkrg"Eq"4" cv "f qr gf "VkQ4"hkro u'i tqy p"qp"T/CnQ5"uwdutcvg0'O ci pgvk"o qo gpv'y cu" hqwpf "cu"2053" D" hqt"twkrg" f qr gf "VkQ4"qp"Uk'uwdutcvg"cpf "2045" D" hqt"cpvcug"

NcCrQ<sub>5</sub>" uwdutcvg" ]J qpi " gv" crf' \*4226+\_0' Cf qr vki " th/o ci pgtqp" ur wwtkpi " vgej pls wg." Igqpi "gv'crf'\*4227+" hqwpf "vj g"o ci pglve"o qo gpv'qh"20" D"kp"cpvcug" Eq/f qr gf "hkm "]Igqpi "gv'crf'\*4227+\_0'Y kj "uco g" f gr qukkqp"vgej pls wg." I tkhkp"gv' crf' \*4227+" f go qputcvgf "c"o ci pglve"o qo gpv'qh"30" D"ht"4"cv0 "Eq/f qr gf " VQ<sub>4</sub>" hkm "i tqy p" qp" NcCrQ<sub>5</sub>" uwdutcvg" ]I tkhkp" gv' crf' \*4227+\_0' Tqdgwu" gv' crf' \*422: +"uwf kgf "vj g"ghgev'qh'wmtc/j ki j "xewwo "cppgcrkpi "qh'Eq"\*5"cv0 +"f qr gf " cpvcug" VQ<sub>4</sub>" hkm u" f gr qukgf " qp" NcCrQ<sub>5</sub>" uwdutcvg" d{ " vj g" chqgo gpvkpgf " vgej pls wg" ]Tqdgwu" gv' crf' \*422: +\_0' Vj g{ " erko gf " cp" kpetgcug" kp" o ci pglve" o qo gpv'htqo "207" D"cu" f gr qukgf "+"vq"208: " D"wpf gt"vj g"xewwo "cppgcrkpi " eqpf kkp0'

"O ci pglve"o qo gpv'y cu'htvj gt'hqwpf "vq" f getgcug'htqo "206"vq"2024" D"\*z" ?"20248"vq"2034+"ht"cpvcug"cu'y gm'cu'twkg" hkm u'htqo "2076"vq"2026" D"\*z"?" 20248"vq"2038; +kp"ecug"qh'Eq/f qr gf "hkm u'wulpi "o ci pgtqp"ur wwtkpi "]O k'gv'crf' \*422; +\_0C"j ki j guv'f qr cpvr' gtegpvc i g'c'42""y cu'tgr qtvgf "d{ "Qucf c"gv'crf'\*4228+" hqt" Eq/f qr gf " VQ<sub>4</sub>" pcpquj ggu" f gr qukgf " " qp" s wctv " qt" Uk" uwdutcvg" y kj "c" o cti kpcmf " rguu" o ci pglve" o qo gpv' qh' 306" D'0' Uwt{cpcptc{cp" gv' crf' \*4227+" qdugtvgf "cp" kpetgcug"kp"o ci pglve"o qo gpv'htqo "207" D"vq"2058" D'o gcuwtgf "cv" 4222"Qg"ht"vj g"5"cv "Eq/f qr gf "VQ<sub>4</sub>" hkm u" f gr qukgf "d{ "uqni gn'ur kp"eqcvkpi 0' Hqt" vj g" uco g" Eq" eqpegpvtvqp." Hw" gv' crf' \*4228+" cpf " \ j cpi " gv' crf' \*4228+" tgr qtvgf "o ci pglve"o qo gpv'qh"206" D"cpf "205: " D."tgr gevkgf "j cxkpi "uco g" cpvcug" r j cug" i tqy p" qp" NcCrQ<sub>5</sub>" uwdutcvg" wulpi "RNF" vgej pls wg" ]Hw' gv' crf' \*4228+" \ j cpi "gv'crf'\*4228+\_0'C"s wkg"iqy "o ci pglve"o qo gpv'qh"20288" D'y cu" qdugtvgf "ht" f qr gf "cpvcug" pcpqhktgu" vj cv' f getgcug"vq"20269" D"ht" twkg" pcpqhktgu" i tqy p" d{ " grgetqr kppkpi " o gj qf " ]Ik" gv' crf' \*4229+\_0' O ci pglve" o qo gpv' y cu" cnq" xctkgf " htqo " 207" vq" 208" D." hqt" hkm u" f gr qukgf " d{ " grgetqej go kcn' f gr qukkqp" vgej pls wg" ]Y cpi " gv' crf' \*4229+\_0' J w' gv' crf' \*422: + f go qputcvgf "c"o ci pglve"o qo gpv'qh"307" D"kp"9"cv0 "Eq/f qr gf "twkg" hkm " f gr qukgf "qp" e/ucr r j ktg" uwdutcvg" wulpi "RNF" vgej pls wg' Qp" uko kct " uwdutcvg." Hwwo wtc"gv'crf'\*422: +"uj qy gf "cp" kpetgcug"kp"o ci pglve"o qo gpv'htqo "30"vq"307" D"ht" Eq"7"cpf "32"cv0 "tgr gevkgf "d{ "O DG" vgej pls wg' Kp" ecug"qh'cpvcug" pcpqr ctvkgu" u{pvj guk gf " d{ " j {f tqy gto cn' vgej pls wg." Rgtgktc" gv' crf' \*422: +

uj qy gf "cp"cpqo cmwu"dgj cxkqwt0'Y kj "kpetgcug"kp"Eq"eqpegpvtcvkqp"htqo "5"vq"  
 9"cv0 . "vj g"o ci pgvke"o qo gpv'y cu"gpj cpegf "htqo "204"vq"208" d0J qy gxgt. "y kj "  
 hwtvj gt"lpetgcug"kp"Eq"eqpegpvtcvkqp. "vj g"o ci pgvke"o qo gpv'f getgcugf "htqo "206"  
 vq"208" d"]Rgtgkct"gv'cr0\*422: +\_0'C"o ci pgvke"o qo gpv'qh"2056" d"y cu"qdugt xgf "  
 d{"O eEnmtg"gv'cr0\*422: +"kp"vj g"cu"i tqy p"vj kp"hkro "qh"Eq/f qr gf "VlQ4"d{"rks wkf "  
 r tgewtuqt"o gvcn'qti cple"ej go kecn'xcr qwt" f gr qukklqp"vgej pls wg"]O eEnmtg"gv'cr0"  
 \*422: +\_0' J qy gxgt." chvgt" r quv" cppgcrkpi " qh" vj g" hkro u." hgttqo ci pgvkuo " y cu"  
 xcpluj gf "]O eEnmtg" \*422: +\_0' Cppgcrkpi " qh" Eq" qp" VlQ4" twkng" hkro u" rnf " vq" c"  
 hgttqo ci pgvke"o qo gpv'qh"20 " d"][ cp"gv'cr0\*422; +\_0'[ co cucnk'gv'cr0\*422; +"  
 qdugt xgf "c"j ki j "o ci pgvke"o qo gpv'qh"5" d"kp"Eq/f qr gf "VlQ4"hkro u"i tqy p"qp"  
 i rnuu"uwduxcvg0D{"uqn'i gn'ur kp"eqcvkpi "o gjv qf ."o ci pgvke"o qo gpv'y cu"hqwpf "vq"  
 dg" 30 " d" hqt"Eq/f qr gf "hkro u"]Z w' gv'cr0\*4232+\_0'C"ej cpi g"kp"r j cug"htqo "  
 cpcvcug" hqt"Eq"40"cv "vq" cpcvcug"cpf "twkng"o kzgf "r j cug" hqt"Eq"32"cv0 "y cu"  
 qdugt xgf "y kj "c"uwdugs wgpv'lpetgcug"kp"o ci pgvke"o qo gpv'htqo "204: " d"vq"205: "  
 d"kp"ecug"qh"ur tc{r {tqn{| gf "VlQ4"hkro u"i tqy p"qp"s wctv "uwduxcvg"]Uj cto c"gv"  
 cr0\*4232+\_0'Ghgev"qh"r quv" cppgcrkpi "y cu" f luewuugf "d{"I qj "gv'cr0\*4233+"hqt"7"  
 cv0 "Eq/f qr gf "VlQ4"hkro u" f gr qukkgf "qp"Ut VlQ5\*223+"uwduxcvg"d{"rks wkf "r j cug"  
 f gr qukklqp"o gjv qf 0'

Ukpi j "gv'cr0\*4234+"uwf kgf "vj g" hgttqo ci pgvkuo "qh"eqdcn'f qr gf "cpcvcug"  
 VlQ4"vj kp" Lm u" wulpi "grgo gpv'ur gekle"Z O EF "cv"vj g"Eq" N4.5"gf i gu"kp"dqvj "vj g"  
 uwthceg" ugpuklxg" vqcn' grgevtqp" {kgrf " \*VG[ +" cpf" dwm' ugpuklxg" vqcn'  
 hwtguegpeg" {kgrf " \*VH[ +"o qf gu0'Vj g" rcti g"o ci pgvke"o qo gpv'qh"vj g"Eq" kqpu."  
 208/406" μB lEq." y cu" qdugt xgf " d{" vj g" VH[ " o gjv qf 0' Vj g" qtki kp" qh"  
 hgttqo ci pgvkuo " cv" tqo /vgo r gtcwtg" kp" cpcvcug" Vl3/zEqzQ4/ " y cu" hwtvj gt"  
 uwr r qtvgf " d{" vj g" Z O EF" uwf {" qh" vj g" uco r ngu" y kj " f khtgpv' ecttkgt"  
 eqpegpvtcvkqp0'Vj g{"qdugt xgf ."vj g"r qukklqpu"qh"Eq<sup>4</sup> "cvqo u'uggo "vq"dg" f kur rnegf "  
 htqo "vj g"tgi wct"Vl<sup>6</sup> "ukgu"ecwulpi "tcpf qo "et {uvcn' Lgrf u0'Vj g"o ci pgvke"o qo gpv'



**Fig.2.2** O/J " qh" V<sub>k07Eq207Q4/</sub> " \*c+" O gvcnle." kpvto gf kvq." cpf " kpuwrcvpi " cpcvcug"uco r ngu0\*d+O gvcnle"twkrg"uco r rg"]Chvgt"Ukpi j "gv'cr0\*4234+\_"

xcmgu" f gf wegf "y kj "vj g"VG[ "o qf g"ku"hwqpf "vq"dg">205n"μ<sub>B</sub> Eq."kpf kvcvpi "vj g" r tvguppeg" qh" c" o ci pgvkecm{ " f gcf " r {gt" qh" c7" po " vj kempguu" cv" vj g" uco r rg" uwthcegu0' Vj g" tguwmu" uj qy gf " cpcvcug" V<sub>k07Eq207Q4/</sub> " k" ku" o gvcnle" r j cug" f go qpuctcvpi " j ki j gt" o ci pgvke" o qo gpv" vj cp" vj g" kpuwrcvpi " cpcvcug" cpf " o gvcnle"twkrg"r j cug"\*Hki 040+"Ukpi j "gv'cr0\*4234+\_0'

### Fe doped TiO<sub>2</sub>

k" Hg" f qr gf "twkrg"V<sub>kQ4</sub>. "c" pgi rki kdrg"ej cpi g"kp" o ci pgvkuvcvqp"htqo "40" vq"406"μ<sub>B</sub> IHg"y cu"qdugtxgf "d{ "xct{ kpi "vj g" Hg"eqpegpvcvqp"htqo "2024"vq"202: "kp" hko u'i tqy p"qp" /C<sub>n</sub>Q<sub>5</sub>"uwdutcvg"]Y cpi "gv'cr0\*4225+\_0Cpcvcug" Hg" f qr gf "V<sub>kQ4</sub>" pcpqr ctvkgu"r tgr ctgf "d{ "ej go kecn"uqnwkp" o gj qf "uj qy gf "o ci pgvke" o qo gpv" c20289"μ<sub>B</sub> IHg"cv"cp"cr r dfg" hgrf "qh"3Vgure"]Ngg"gv'cr0\*4226+\_0J qy gxgt. "Y cpi " gv'cr0\*4227+"uj qy gf "r ctco ci pgvkuo "kp" Hg" f qr gf "V<sub>kQ4</sub>. "y kj "Hg"wr vq"42"cv "kp" cpcvcug"cpf "twkrg" o kzgf "r j cug"r qy f gt"uco r ngu"r tgr ctgf "d{ "qz kf cvkxg"r { tqn{uku" o gj qf "]Y cpi "gv'cr0\*4227+\_0Vj g"j ki j guv" gxgt" o ci pgvke" o qo gpv"qdugtxgf "kp" Hg" f qr gf "V<sub>kQ4</sub>" pcpqr ctvkgu"y cu"807 μ<sub>B</sub> IHg" hqt" cpcvcug" f qr gf "pcpqr ctvkgu" u{ pyj guk gf " d{ " o letqgo wnwkp" vgej pks wg" ]Tqf tki wg/ Vqttgu" gv' cr0' \*422: +\_0' Dcr pc" gv' cr0' \*4234+" f go qpuctcvg" hgttqo ci pgvkuo "kp" 6" cv0 " Hg" f qr gf "V<sub>kQ4</sub>" hko u" qp" NcCrQ<sub>5</sub>" uwdutcvg" d{ "RNF" " vgej pks wg0' Uwtc{ pctc{cp" gv' cr0' \*4227+" uwf kgf "vj g"tqrg"qh"xcewwo "cppgcrkpi "qp" Hg" f qr gf "V<sub>kQ4</sub>" \*Hg"2027+" hko u"kp" dqj " cpcvcug"cpf "twkrg" hqto u'f gr qukgf "qp" e/czku" qtkgpvgf "ucr r j ktg" uwdutcvgu0'Y j kg"



vj g'o ci pgvke"o qo gpv'qh'vj g'cu'r tgr ctgf "cpcvcug" hko "y cu'gpj cpegf "htqo "2025" vq" 2068"  $\mu_B$  IHg. "kp" ecug" qh" twkng" hko u. "vj g'o ci pgvke" o qo gpv' y cu' hqwpf "vq" f getgcug"htqo "202; "vq"20236" $\mu_B$  IHg"wpf gt"xcewwo "cppgcrkpi "]Uwt {cpcptc {cp"gv' crf}\*4227+\_0'Ngg"cpf "Mko " \*4229+"uj qy gf "vj cv'o ci pgvkucvkqp"kpctgcug"vgr"vko gu" \*2025"vq"2055"  $\mu_B$  IHg+"hqt"Hg"f qr gf "VlQ4"\*z"? "2023+"wpf gt"xcewwo "cppgcrkpi " ]Ngg" cpf " Mko " \*4229+\_0' Hwtvj gt." Hcp" gv' crf' \*422: +" qdugtvgf " vj g" tqng" qh" cwo qur j gtg"qp"twkng"dcn'o kmgf "r qy f gt"uco r ngu'Vj g"Hg"f qr gf "r qy f gt"\*Hg"? " 606"cv0 +"kp"ckt"eqpf kkp"j cf "uj qy p"vj g'o ci pgvke"o qo gpv'20237" $\mu_B$  IHg"vj cv' f getgcugf "vq"202; " $\mu_B$  IHg"kp"r t gugpeg"qh"Q4"]Nkp"gv'crf'\*422: +\_0'Wr qp"cppgcrkpi " kp"qz {i gp"cv0 qur j gtg."Dcr pc"gv'crf'qdugtvgf "c"f getgcug"kp"o ci pgvkucvkqp"cu"c" uli pcwtg"qh" cppgcrkpi " qh" qz {i gp"xcepekgu"]Dcr pc" gv' crf' \*4234+\_0' Kp"j ki j " gpgti {"dcn'o kmgf "twkng"r qy f gt"qh"Hg"f qr gf "VlQ4"\*Hg"? "2026+"vj g'o ci pgvke" o qo gpv'y cu' hqwpf "vq"dg"¢"2037" $\mu_B$  IHg"]Zkcq {cp"gv'crf'\*4228+\_0'Hqt"Hg"f qr gf " cpcvcug" VlQ4"pcpqr ctveng"y kj "Hg">"4"cv0 . "hgttqo ci pgvkuo "y cu'qdugtvgf " ]\ j w'gv'crf'\*4229+\_0'Twkng"pcpqtqf u"qh"Hg"f qr gf "VlQ4"ht"Hg"eqpegpvcvkqp"¢"5" cv0 "f go qpwtcvgf "hgttqo ci pgvkuo "cv'tqqo "vgo r gtcwtg"]O gri j k'cpf "DqW kcpg" \*422: +\_0' C" tqdwv' o ci pgvke" o qo gpv' ¢509"  $\mu_B$  IHg"y cu' hqwpf "hqt" cpcvcug" Hg" f qr gf " VlQ4" hko u" y kj " 37" cv0 " qh" Hg" f gr qukvf " d {" tgcevxg" o ci pgtqp" ur wwtkpi "]O gpi "gv'crf'\*4229+\_0'Tgegpw{. "Ucpvctc"gv'crf'\*4236+"gZR mkpof "vj g" hgttqo ci pgvkuo "kp"Hg"f qr gf "VlQ4"pcpqtqddqpu"ceeqtf kpi "vq"DO R"o qf gn'vj cv' kpenf g"cp"grgextqp"meem{"vcr r gf "d {"cp"qz {i gp"xcepe {0'Y kj "vj g"vcr r gf " grgextqp"qeewr {kpi "cp"qtdkcn'qxgtrcr r kpi "y kj "vj g"vpr cktgf "grgextqp"\*5f<sup>3</sup>+"qh"c" Vk<sup>5</sup> "kqp" cpf lqt" vj g" vpr cktgf " grgextqp" \*5f<sup>7</sup>+" qh" c" Hg<sup>5</sup> "kqp" ku' hqwpf " vq" dg" tgr qpukng"ht"vj g"hgttqo ci pgvke"qtf gt"]Ucpvctc"gv'crf'\*4236+\_0'Uko kct"DO R" o qf gn'j cu'dggp"wgf "vq"gzr mkp"vj g"qdugtvgf "hgttqo ci pgvkuo "kp"Hg"f qr gf "VlQ4" pcpqr qy f gtu"]P cxcttq"gv'crf'\*4236+\_0'

**Cr doped TiO<sub>2</sub>**

Y cpi " gv' crf' \*4226+" tgr qtvgf " hgttqo ci pgvkuo " kp" 8" cv0 " Et" \*cpv'hgttqo ci pgvke+"f qr gf "twkng"VlQ4"f gr qukvf "qp"T/r m'pg"ucr r j ktg"uwduvcvg'0 Y kj "kpctgcupki "Et"eqpegpvcvkqp."vj g"ucwtcvkqp"o ci pgvkucvkqp"f getgcugf "htqo " 40 "  $\mu_B$  IEt'Vj g"xctkcvkqp"kp"o ci pgvke"o qo gpv'y cu'qdugtvgf "kp" cpcvcug"VlQ4"

hko "f gr qukgf "qp"NCQ"cpf "UVQ"uwdutcvgu"htqo "2027"vq"2028" $\mu_B$  IEt"]Mcur ct"gv" crf0\*4227+0'Cppgcrkpi "Et"f qr gf "VkQ4"co qtr j qwu"hko u"cv"522"Å"tcpuhtqo gf " vj go "vq"cpvcug"et {ucmkpg"r j cug"f guxtq {kpi "vj g"qdugtxgf "hgttqo ci pgvkuo "y kj " 20543" $\mu_B$  IEt"]Y cpi "gv" crf0\*4228+0\ j cpi "gv" crf0\*422: +" uwf kgf " vj g" tqrg"qh" qz {i gp"r ctvkn'r tguamtg"qp"Et"f qr gf "VkQ4"hko u" f gr qukgf "qp"i rnuu"cpf "ner vqp" uwdutcvg"d { "eq/ur wwtgkpi "o gj qf 0'D { "f getgcukpi "vj g"qz {i gp"r tguamtg"htqo "2" vq"2028"Rc."vj g"o ci pgvkuo"y cu"hwf "vq" f getgcug"htqo "2064"vq"202;  $\mu_B$  IEt." t gur gevknq "hqt "Et"ç"20270'

**Mn doped TiO<sub>2</sub>**

O p" f qr gf "VkQ4"twkrg"hko u" f gr qukgf "qp" /CnQ5"uwdutcvgu"d { "RNF " vgej pls wg"uj qy gf "hgttqo ci pgvkuo "cv"tqqo "vgo r gtcwtg"]Y cpi "gv" crf0\*4226+0' Y kj "kpetgcug"kp"O p"eqpegpvcvkp"htqo "4"vq": "cv0 ."o ci pgvke"o qo gpv'y cu" kpetgcugf "htqo "2027"vq"20 5"  $\mu_B$  IO p0Hwtj gt" kpetgcukpi "vj g"O p"eqpegpvcvkp"vq" 34"cv0 ."tgf wegf "vj g"o ci pgvke"o qo gpv"vq"2026  $\mu_B$  IO p"]Y cpi "gv" crf0\*4226+0' Qp" vj g" eqpvtct { ." Uj cto c" gv" crf0\*4233+" qdugtxgf " cp" kpetgcug" kp" o ci pgvke" o qo gpv"htqo "2029" $\mu_B$  "vq"2023" $\mu_B$  IO p"y kj "kpetgcug"kp"O p"eqpegpvcvkp"htqo " 2022"vq"2027"]Uj cto c"gv" crf0\*4233+0'Z w"gv" crf0\*4228+"g zr rqtgf "vj g"xctkcvkp"kp" o ci pgvke"o qo gpv'y kj "r j cug"qh"32"cv0 "O p" f qr gf "kp"VkQ4"hko u" f gr qukgf "d { " uqn'i gn'ur kp"eqcvkpi "o gj qf 0'Vj g"o ci pgvke"o qo gpv'y cu"hwf "vq"ç"2029" $\mu_B$  IO p" hqt"cpvcug"r j cug"y j gtgcu"30" $\mu_B$  "IO p" hqt"twkrg"]Z w"gv" crf0\*4228+0'Hwtj gt."vj g" o ci pgvke"o qo gpv'y cu" kpetgcugf "htqo "2027"vq"3" $\mu_B$  IO p"wr qp"cppgcrkpi "]Z w"gv" crf0\*422: +\_"

**Cu doped TiO<sub>2</sub>**

P qpo ci pgvke"E w'f qr gf "VkQ4"uj qy gf "tqqo "vgo r gtcwtg" hgttqo ci pgvkuo " ]F vj cfr g" gv" crf0\*4227+." \ j gpi " gv" crf0\*4236+0' F vj cfr g" gv" crf0' f go qputcvgf " hgttqo ci pgvkuo " kp" RNF " i tqy p" hko u0' Vj g"o ci pgvke" o qo gpv'y cu" hwf "vq" dg"30' D"IEw'cvqo "y j kej "ku'uki p hiecpv\ "rti g0'Vj gqtgvkecn'ecrwcvkpu"uwi i guv' rti g"o ci pgvke"o qo gpv'ecp"qpn\ "dg'r qukdrg"kh'cp"qz {i gp"xcepe { "ku'ukwcvgf "kp" vj g"pgctguv"pgki j dqt"uj gm'qh"Ew0'K' uwi i guu"vj g"tqrg"qh"qz {i gp"xcepekgu"ku" etwecn" hqt" vj g" cr r gctcepeg" qh" hgttqo ci pgvkuo 0' Vj gug" qz {i gp" xcepekgu" ctg" hcxqwtgf "d { "E w'f qr kpi "]F vj cfr g"gv" crf0\*4227+0'kp"cf f kkp." \ j cpi "gv" crf0\*4236+ "

uwi i guvgf "vj g'hgttqo ci pgvkuo "kp"Ew'f qr gf "cpcvcug"VkQ4"hkro u'ku'f wg"vq'i tckp" dqwpf ct { "f ghgeu0

Vj g"qz {i gp" f ghgeu" ecp" dg" vj g" f qo kpcvkpi "hcevt" hqt" kpetgcukpi " vj g" ucwvcvkqp"o qo gpv'qh'vj gug'Ew'f qr gf "VkQ4"hkro u0'Vj gug'tguwmu'engctn{ "uwi i guv" vj g'ko r qtvcpv'tqng"qh'qz {i gp"xcecpelgu"kp"ftkxkpi "vj g'hgttqo ci pgvkuo "] \ j gpi "gv" cr0' \*4236+\_0' Vj gqtgvkcm{ . "Gttleq" gv' cr0' \*4227+" uwf kgf " vj g" ghgeu' qh' qz {i gp" xcecpelgu"qp"vj g'hgttqo ci pgvke'r tqr gt vku'qh"VkQ40'Vj gkt'r t gugpeg'y cu'hqwpf "vq" f getgcug"vj g"gpgti { "tgs wktgf "vq"kpvtqf weg"vj g"ko r wtkkku"kp"vj g"j quv'rwkleg"cpf " j gpeg'r t gugpeg'qh'ko r wtkkku'ctg'tgrvcgf "vq" c'j ki j gt"xcecp{ "eqpegpvcvkqp0

**Ni doped TiO<sub>2</sub>**

J qw'gv'cr0'\*4229+"tgr qtvgf "hgttqo ci pgvkuo "kp"P k'f qr gf "cpcvcug"VkQ4"\*z" ?"204."206."208."20: +"f gr qukgf "qp"UkQ4"d{ "tgcvcxg"o ci pgtqp"ur wwtkpi 0' Y kj "kpetgcug"kp"P k'eqpegpvcvkqp."ucwvcvkqp"o ci pgvkucvkqp'y cu'kpetgcugf 0'Vj g" ucwvcvkqp"o ci pgvkucvkqp'y cu'hqwpf "dgy ggp"203"vq"30"μ<sub>B</sub> IP k'hqt"Q4"cppgcrkpi cpf" 209" vq" 30: μ<sub>B</sub> IP k' hqt" Ct cpggcrkpi " eqpf kkp0' Uq." k' ku" gxkf gpv' vj cv' cpggcrkpi " wpf gt" qz {i gp" f ghkcpvltgf welpi " eqpf kkp" \*cpggcrkpi " wpf gt" Ct+." ngcf u" vq" hqto cvkqp" qh' qz {i gp" xcecpelgu" vj cv' kpetgcugu" vj g" hgttqo ci pgvke" o qo gpv'J qw'gv'cr0'\*4229+\_0'Ej q"gv'cr0'\*4228+"qdugtvgf "hgttqo ci pgvkuo "kp"P k' f qr gf "VkQ4"d{ "uqn'i gn'o gy qf "hqt"P k'eqpegpvcvkqp"3"vq": "cv0 " ]Ej q"gv'cr0' \*4228+\_0'

**V doped TiO<sub>2</sub>**

C" j ki j " o ci pgvke" o qo gpv' c6045 μ<sub>B</sub> IX" y cu" tgr qtvgf " d{ " J qpi " gv' cr0' \*4226+"kp"X"\*7"cv' +"f qr gf "VkQ4"hkro "f gr qukgf "qp"NcCrQ5"uwdutcvg0'Vkp"gv'cr0' \*422: +"f go qputcvgf "hgttqo ci pgvkuo "kp"X" f qr gf "VkQ4"pcpqr ctvengu"kp" cpcvcug" hqto "u{pvj guk gf "d{ "uqn'i gn'vgej pks wg'y kj "z"? "2"vq"2080'

**Al doped TiO<sub>2</sub>**

Y cpi " gv' cr0' \*4236+" f go qputcvgf "hgttqo ci pgvkuo "kp" Cn' f qr gf "twkng" VkQ4"vj kp"hkro u'i tqy p"qp"CnQ5"uwdutcvgu"d{ "RNF "vgej pks wg'y kj "V<sub>e</sub>"pgct"562" M0'Vj g"O<sub>u</sub> y cu'hqwpf "vq"dg"208: . "209: "cpf"205"μ<sub>B</sub> / V" hqt"4."8"cpf": "cv0 " Cn" tgr gevkgng{ 0'O ci pgvke"o qo gpv'cuuqekvgf "y kj "vj g" hqto cvkqp"qh"Vk<sup>5</sup> "kpu"y cu" hqwpf "kp" cm' ecugu" dw" vj g{ "eqwr ng" f hgtgpv{ "cu" c" tguwn' uj qy kpi " f hgtgpv"

o ci pgvle" o qo gpw0 Vj g" o ci pgvkuo "ku" uw r qugf "vq" dg" cuuqekcvgf "y kj " vj g" grgevtpu" i gpgtcvgf " d{ " vj g" qz {i gp" xcepe{ " wr qp" Crif qr kpi 0Vj g" grgevtpu" cuuqekcvgf "y kj " vj g" f ghgev" qeewr kgu" pgctd{ " Vk' ukvgu" ngcf kpi "vq" hqto cvkqp" qh" V<sup>5</sup>- "cpf " cv" vj g" uco g" vko g." kv" ur cvkcm{ " gzvpgf " vj g" y cxg" hwpevkqpu" cuuwtkpi " qxgtncr r kpi " dgvy ggp" pgki j dqwtu" vj cv" o c{ " vj g" tgcucp" dgj kpf " vj g" tqqo " vgo r gtcwtg' hgttqo ci pgvkuo "]Y cpi "gv'cr0\*4236+\_0'

**Nb doped TiO<sub>2</sub>**

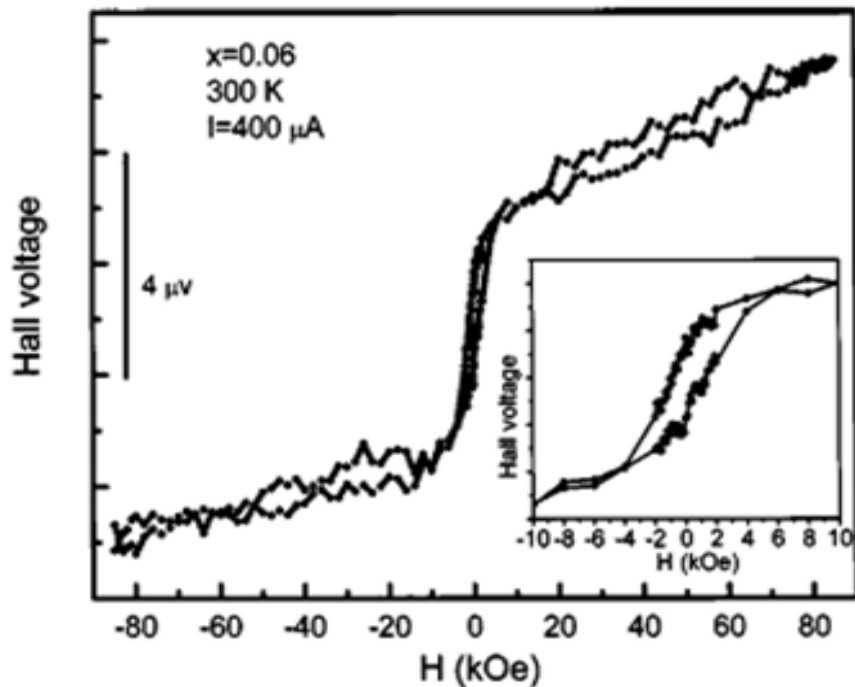
Vj g" o ci pgvle" ghgev" y cu" uwf kcf " kp" pppo ci pgvle" P d" \*7" cv" +f qr gf " V<sub>4</sub>Q" vj kp" hko u" f gr qukvf " d{ " RNF 0' " Kpungcf " qh" o ci pgvle" o gcuwtgo gpw. " vcpur qtv" cpf " o ci pgvq/vcpur qtv" o gcuwtgo gpw" tngxgcrf " vj g" rtgugpeg" qh" o ci pgvle" o qo gpw" kp" vj g" u{ uvg0 0Vj g" gzvtpule" hcevqtu" hqt" vj g" hgttqo ci pgvkuo " y cu" flectf gf " cpf " uwi i guvf " vj cv" f qr kpi " pppo ci pgvle" grgo gpw" kp" c" pppo ci pgvle" j quv" o c{ " vckqt " vj g" o cvgtkcn" r tqr gtv{ " y j lej " qr gpu" wr " pgy " cxgpwgu" hqt" f ghgev" kpf wegf " o ci pgvkuo " hqt" vj g" r quukdr" ur kvtqpkcu" cr r rlecvkpu0' ]\ j cpi "gv'cr0\*422; +\_0'

**2.2 Transport Properties**

Grgevlecn" r tqr gt vku" qh" V<sub>4</sub>Q" vj kp" hko u" ctg" hqwpf "vq" f kht" uki pkkcpcv{ " htqo "cpcvcug" vq" twkng" r j cug0 Tgukvkv{ "cpf "J cm/ghgev" o gcuwtgo gpw" uj qy gf " cp" kpuwrcvt/o gvcn' vcpukvqp" kp" c" f qpqt" dcpf " kp" cpcvcug" vj kp" hko u" y kj " tgrvkvgn{ " j ki j " f qpqt" eqpegpvcvqpu"]Vcpi "gv'cr0\*3; ; 6+\_0J qy gxgt. "hqt" uko kct" f qpqt" eqpegpvcvqpu. " vcpukvqp" y cu" pqv" qdugtvgf " kp" twkng" vj kp" hko u0' K' uki pkkgu" c" rcti gt" ghgevkvxg" Dqj t" tcf kwu" qh" f qpqt" grgevtpu" kp" cpcvcug" vj cp" kp" twkng" eqpugs wgpv{ " j cxkpi " c" uo cmgt" grgevtpu" ghgevkvxg" o cuu0' Vj g" uo cmgt" ghgevkvxg" o cuu" kp" cpcvcug" ku" eqpukvgpv" y kj " vj g" j ki j " o qdkkv{ " t gur qpukdr" hqt" dcpf " rknng" eqpf wevkp0' K' ku" cnq" t gur qpukdr" hqt" vj g" xgt { "uj cmqy " f qpqt" gpgti kgu" kp" cpcvcug" r j cug" ]Vcpi "gv'cr0\*3; ; 6+\_0'

Y cpi "gv'cr0\*4225+" kpxguki cvgf " twkng" Hg<sub>z</sub> V<sub>5/2</sub> Q<sub>4/</sub> " \*z" ? "204. "208. "cpf " 20: +vj kp" hko u" i tqy p" qp" /C<sub>4</sub>Q<sub>5</sub>" uwdutcvgu" d{ "RNF "]Y cpi "gv'cr0\*4225+\_0Vj g" vgo r gtcwtg" f gr gpf gpv" t gukvkv{ "y cu" pgctn{ "o gcmle" cv" tqo "vgo r gtcwtg" dw" dgj cxgf " rknng" ugo leqpf wevkpi " cv" nqy gt" vgo r gtcwtgu0' Vj g" gzvctqtf kpcet { "J cm' ghgev" y j lej " ku" rvgt" vgo gf " cu" cpqo cnqwu" J cm' ghgev" qpg" qh" vj g" ng{ "

ej ctcevgtkukleu"qh"vj g"hggtqo ci pgvle"ugo kqpf wevqt"y kj "eqgtekxkkgu"uko krt"vq" vj g"j {uvgtguku"ewtxgu"kp"o ci pgvle"o cvgtkcn'y cu"qdugtxgf "cv"tqqo "vgo r gtcwgt" ]Hki 040\_0' Vj g" j {uvgtguku" uki pklgf " vj g" kvgtcevkap" qh" kkpgtcpv' ecttkgtu" cpf " mcecrik gf "grgevtqp"ur kpu"qh'Hg'kpu0Vj g'ecttkgtu'y gtg'hqwpf "vq"dg"qh'r 'v{r g'y kj " c" ecttkgt" f gpuk{ " qh" cdqw"  $32^{44}$  leo  $5$ ." ]Y cpi " gv" cr0'  $*4225 \pm 0$  " Vj g" o ci pgvq/ tgukucpeg" \*O T+'y cu"cdqw"vq"dg"7' "cv'4'M\*B 7"V'hkgrf +'cpf 'k'dgeco g'pgi cvkxg" \*rguu'vj cp'208' +'y j gp"o gcuwtgf "cv'tqqo "vgo r gtcwgtg0'



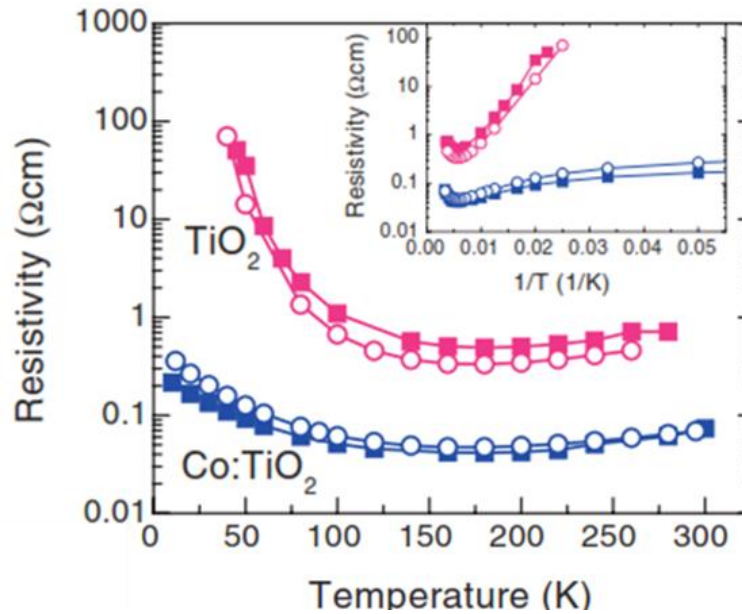
**Fig.2.3** J cm'xqnci g'xgtuwu"cr r ngrf "o ci pgvle"hggrf "cv'522"M'hqt"z"? "2080'Vj g" gzvcqtfkpct{ " J cm' ghgev" f qo kpcvgu" cv" mpy " hgrf u" cpf " uj qy u" j {uvgtgve" dgj cxkqwt"cu'uj qy p'kp"vj g'kpugv']Chgt"Y cpi "gv'cr0'  $*4225 \pm$

Uj kpf g" gv" cr0'  $*4225 \pm$  tgr qtvgf " vj g" vtcpur qtv" cpf " o ci pgvqvcpur qtv" r tqrgtvgu" qh"  $V_{kQ_4}$  cpf "  $V_{kQ_0}$ ;  $E_{q_{203}Q_{4/}}$  " hkm 0' Vj g" J cm' ghgev" o gcuwtgo gpvu" uj qy gf "p/v{r g"eqpf wevkap"kp"dqj "Lm u'y kj "guko cvgf "ecttkgt"eqpegpvcvkapu" qh"  $\phi 306$  "z"  $32^3$ : " cpf "  $408$  "z"  $32^3$ : leo  $5$ ." tgr gevkxgn{ " cv'522" M0' Vj g" eqpf wevkap" o gej cpkuo "y cu"awi i guvgf "vq" dg"eqo r ngvgn{ "f wg"vq" vj g" r tgugpeg" qh" qz {i gp" xcecpelgu"vj cv'kpvtf weg"ucvgu'lwu'v'dgny "vj g"eqpf wevkap"dcpf 0'Vj g" f khgt gpeg" kp'tgukvkvk{ "qh'r vtg"cpvcug"  $V_{kQ_4}$  "ecwugf "d{ "Eq"uwdurkwwkqp"o c{ "qeewt "f wg"vq" xcecpel{ "r qr wrcvkap"vq"ucvkuh{ "ku"xcrpeg" \*Eq $^4$  "cu"y gm'cu"ku"eqpvtkdwwkqp"vq"

o ci pgve"uecwtgkpi 0'kpetgcug"kp"tgukukxkv{ "kp"ur kvg"qh"cp"lpetgcug"kp"ecttktg"  
 eqpepvtcvkqp"uwi i guu"ftqr "kp"o qdkrkv{ "f vgw"vq"o ci pgve"qt"utckp"uecwtgkpi "  
 rtqeguugu0 Vj g" O T" y cu" hqwpf " vq" dg" r qukkxg" cpf " ku" uki pkhecpv' cv' nqy "  
 vgo r gtcwtg"vj cv'eqttgur qpf "vq"eqpf kkpapu"tgr tgugpvkpi "r ctvkn"kpkk cvkqp"qh"  
 uj cmqy "f qpqt"ucvgu."eqo o qpn{ "cwtkdwgf "vq"qz {i gp"xcecpckgu"}Uj kpf g"gv'cr0'  
 \*4225+\_0' Vj g" hgttqo ci pgvkuo " qdugt xgf " kp" vj g" u{vgo u" tgs wktgu" vj g"  
 eqphko cvkqp"qh"kvtkpule"pcwtg"qh"o ci pgvkuo 0'Gctnktg"kv'y cu"dgrkxgf "vj cv'  
 qdugt xcvkqp" qh" cpqo cmwu" J cm' ghgev' \*CJ G+" eqphko u" vj g" kvtkpule"  
 hgttqo ci pgve"dgj cxkqt"}Uj kpf g"gv'cr0'\*4226+\_0J qy gxgt."Uj kpf g"gv'cr0'\*4226+ "  
 uj qy gf "vj cv'gxgp"rtgugpeg"qh'envvgtu"qh"Eq"pcpqr ctvkn"kp"vj g"Eq/f qr gf "  
 VkQ4"ecwugu"CJ G0J gpeg."vq"eqpenmf g"vj g"kvtkpule"pcwtg"qh"vj g"hgttqo ci pgve"  
 qtf gkpi "kp"FOU"o cvgtkn"qpg"pggf u"vq"r gthqto "xctkqu"ej ctcevgtk cvkqp"  
 vgej plsvgu"vq"eqphko "vj g"twg"o ci pgvkuo "kp"vj g"u{vgo u0"

Kp"ecug"qh"Eq/f qr gf "cpcvcug"VkQ4"Łm u."Tco cpgvk"gv'cr0'f go qpvtcvgf "vj g"  
 eqpf wekqp"kp"c"o gvcnke"fqqt/ko r vtkv{ "dcpf"y kj "c"uki pcwtg"qh"vj g"Mpfp q"  
 ghgev0 Vj g"tgukukxkv{ " . "o gcuwgf "cv"tqqo "vgo r gtcwtg"y cu" hqwpf "vq" dg" ċ "  
 3 eo "hqt"VkQ4" hkn "y j gtgcu"cp"qtf gt"qh"o ci pkwf g"uo cmgt" hqt"Eq/f qr gf "  
 hkn u0Htqo "Hki 046."kv'ku"erget"vj cv'vj g"nqy "vgo r gtcwtg"\*V+"dgj cxkqt"qh"vj g"  
 f qr gf "Łm u"ku"eqo r ngvgn{ "f khgtgpv'htqo "vj g"wpf qr gf "qpgu0Vj g"kpugv'qh"Hki 046"  
 kpf kecvgu" hqt"vj g"VkQ4" hkn u." "lpetgcugu"gzr qpgpvcn{ "y kj "3 IV'cu"cp"kp kecvkqp"  
 qh'cevxcvgf "vcpur qtv."y j gtgcu" hqt"Eq/f qr gf "Łm u."kv'tgo ckpu"eqo r ctvkn"gn{ "  
 eqpuwcpv' cpf " cm quv' ucwvcvgu" cv' nqy " vgo r gtcwtg0' Vj g" cwj qtu" j cxg" cmq"  
 f kuctf gf "vj g"j qr r kpi "vcpur qtv'o gej cpkuo "kp"vj g" hkn u"cu"r tgxkqun{ "tgr qtvf "  
 kp" twkn" uco r ngu" eqpvckpki "Eq"o gvcn'envvgtu0' J qy gxgt." vj g" j ki j " Mpfp q"  
 vgo r gtcwtg"Vm" ċ342"M"uwi i guu" c" utqpi "kvgtcevkv" dgw ggp"Eq"ur kpu"cpf "  
 eqpf wekqp"grgetqpu"kp"vj g"ko r vtkv{ "dcpf "\*"cp"qtf gt"qh"o ci pkwf g"j ki j gt"vj cp"  
 qdugt xgf "xcnw"kp"o gvcn+"cpf "ko r rku"eqpf wekqp"grgetqpu"cpf "vj g"Eq"nqecn"  
 o qo gpv"ctg"kp"ucvgu"vj cv'ctg"gpgti gvckm{ "emugt"vq"j cxg"utqpi "kvgtcevkv0'  
 ]Tco cpgvk"gv'cr0'\*4229+\_0'

"



**Fig.2.4** Grgevt kecn'r tqr gt vku'qh'cpcvcug'VkQ<sub>4</sub>'cpf 'Eq<VkQ<sub>4</sub>0'Vj g'kpugv'uj qy u'vj g' t gukukxkv{ 'xgtuwu'3 IV'qh'vj g'cpcvcug'VkQ<sub>4</sub>'cpf 'Eq<VkQ<sub>4</sub>0]Chvgt 'Tco cpgk'g'v'c'f0' \*4229+\_'

Uko krc't "Mqpf q" rkn'g" dgj cxkqwt" y cu" qdugt xgf "d{ "Dcr pc" gv'c'f0' \*4234+\_' kp" ecug" qh' V<sub>8/z</sub> Hg<sub>z</sub> Q<sub>4/</sub> "z" ? "2. "206+\_' hko u'f gr qukgf "d{ "RNF 0'Vj g{ "j cxg'uj qy gf "c" eqo r gvkkqp" dgwy ggp" vj g" o ci pgv'e" qtf g'kpi " o ge'j cpkuo " d{ "L<sub>TMM</sub> " cpf " vj g" o qo gpv' uetggp'kpi " o ge'j cpkuo " d{ "L<sub>Mppf q</sub> " kp" xkgy " qh' r qr wrt " F qpkcej " r j cug" f kci tco " ]Tco cpgk'g'v'c'f0' \*4229+\_0'Vj g'eqw r'kpi " dgwy ggp" vj g" r'qec'f0' qo gpv'cpf " vj g'ej cti g'ectl'kgtu" ku" g'xkf g'pegf " h'qo " o ci pgv'qtgukucpeg" o gcuwtgo gpw' qh' vj g' Lm u'0'Qxgtcm" vj g'eqw r'kpi " qh' r'qec'f0' ci pgv'e" o qo gpv'cpf " vj g'ur kp" qh' k'k'p'gtcpv' ectl'kgtu" qr gpu' pgy " cxgpwgu" h'qt " f gh'gev" gpi k'p'gg'kpi " d{ "v'cpuk'kqp" o gvcn'f qr kpi " ]Dcr pc" gv'c'f0' \*4234+\_0'

### 2.3 Low Energy Ion Implantation/ Swift Heavy Ion Irradiation Studies

#### Ko r r'cpv'kqp 'kp' V'kQ<sub>4</sub>'

V'cpuk'kqp" o gvcn' rkn'g" Eq" ]Cnf qi cp" gv'c'f0' \*4228+\_' Mko " gv'c'f0' \*4227+\_' Uj wvj cpcpf cp" gv'c'f0' \*4226+\_' "P K] \ j w' gv'c'f0' \*4228+\_' "O p" cpf "Hg"]5; \_] cxg' dggp" ko r r'cpv'g'f "kp' V'kQ<sub>4</sub>" wukpi " h'qy " gpgti { "kqp" dgco 0' Cnf qi cp" gv'c'f0' \*4228+\_' qdugt xgf " c' h'c'ev'kqp" qh' vj g' Eq" kqp" j cu" dggp" ko r r'cpv'g'f " r tqr g'tn' { "i k'k'kpi " t'kug" v'q" c" r'mpi " t'cpi g' h'gttqo ci pgv'e" qtf g' t" y j gt'gcu" vj g' tgo c'k'kpi " Eq" g'z'k'ku" cu" enw'v'gtu" uj qy kpi "

uwr gtr ctco i pgvle" dgj cxkqwt0'Y kj " c" dgrhgh' qh' f kuuqrxkpi "Eq" enwvgtu" wpf gt" cppgcnkpi .Mko "gv'cr0'\*4227+'j gcv'tgcvvf "vj g'cu'ko r rcpvfg "hko u'cv'; 22"AE"wpf gt" 3z32<sup>8</sup>" Vqtt" qz {i gp" r ctvkn' r tguuvtg0' Hgy "uo cni' Eq" enwvgtu" y gtg" hqwpf "vq" f kuuqrxg"kpukf g"vj g"hko "dw'rcti gt" enwvgtu"y gtg"qdugt xgf "qp"vj g"hko "uwthceg" vj cv'tg'eqo r qugf "qh'o gvcnle"Eq"eqphko gf "d{ "Z O EF "cpf "Z C P G U"]Mko "gv'cr0' \*4227+\_0' J qy gxgt." Uj wvj cpcpf cp" gv' cr0' \*4226+" eqwf "pqv' cdrg" vq" ugg" cp{ "EqIEqQ" r j cug" kp" ko r rcpvfg "hko u" r tqdgt "d{ "grgo gpv' ur gekhle" GZCHU" cpf "Z C P G U' Kpuvgcf "qh" vcpukxqp" o gvcn. "hgttqo ci pgvkuo "y cu' cnuq" qdugt xgf "kp" ukpi rg"et {ucnu"qh"twkng"VkQ4"d{ "ko r rcpvki "kpgtv"kpup"rkng"Ct l'P" o gf kvgf "d{ "rcwleg" f ghgeu"]Et wj "gv'cr0'\*422; +\_0'Cr ctv'htqo "o ci pgvkuo ."grgo gpw'rkng"Et. "X" ]Vengwej k'gv' cr0' \*4222+\_ "cpf "P " ]P co dw'gv' cr0' \*4228+\_ "ctg" cnuq" hqwpf "vq" dg" ko r rcpvfg "kp"VkQ4' hqt "vj g' r quukdrg" r j qvqecvnc{ vlc'cr r rncvkvpu0'

"

**Ktcf kvkqp 'kp'VkQ4'**

Uj Ki'y gtg" wugf "vq" o qf kh{ "vj g" utwewtg" qh"VkQ4" vj kp" hko u'd{ "etgcvkpi " co qtr j k gf " rcpv' v'cemu" r qkp' f ghgeu" f gr gpf kpi " qp" vj g" gpgti { " qh" vj g" r tqlgevkng"kpup"]Kij kney c"gv'cr0'\*4228+\_0'Dgukf gu."co qtr j k cvkqp"qh"VkQ4."Uj Ki' kpf wvgf " et {ucnrk cvkqp" qh" co qtr j k gf " vkcpk" vq" pcpqet {ucnrkpg" r j cug" ]Vj cmwtf guck" gv' cr0' \*422; +\_0' Utwewtcn' r j cug" vcpuhqto cvkqp"htqo "cpcvug" vq" twkng" r j cug"y cu"qdugt xgf "y kj "kqp"ktcf kvkqp"]Tcvj "gv'cr0'\*422; +\_0'Vj cmw"gv'cr0' \*4233+"ktcf kvgf "VkQ4"vj kp" hko u'htqo "i tqy p"qp" /CnQ5"\*2223+'uwdutcvgu"d{ " th'o ci pgtqp"ur wwtkpi "y kj "422"O gX"Ci <sup>37</sup>- "kqpu0'Y kj "c"hwgpeg"qh"7z32<sup>34</sup>" kpukeo <sup>4</sup>."cpcvug" hko "uj qy gf "hgttqo ci pgvkuo "y kj "r j cug"eqpxgtvgf "vq" c"o kz gf " r j cug"qh"twkng"cpf "dtqqnkv0'Vj g'tgf kukt dwkqp"qh'ej cti gu"co qpi "vj g"Vk<sup>5</sup>f"cpf " Q"4r "qtdkcn"uj qy gf "hgttqo ci pgvkuo ."cu"gxkf gpegf "htqo "Z O EF "]Vj cmw"gv'cr0' \*4233+\_0'Twkn"VkQ4"ukpi rg"et {ucnu"y gtg"ktcf kvgf "y kj "4"O gX"Q"kpup"cv'tqqo " vgo r gtcwtg" xct {kpi "vj g"hwgpeg"htqo "3"z32<sup>37</sup>"vq"7z32<sup>38</sup>"kpukeo <sup>4</sup>0'C"Vk<sup>5</sup>- /Qx" f ghgev"eqo r ngz"y cu"i gpgtcvgf "f wg"vq" kqp"ktcf kvkqp0'Vj g"Vk<sup>5</sup>- "kpu"uggo gf "vq" r tqxkf g" nqecn' 5f "o qo gpw" y j lej " ctg" f gekuxgn{ " tgrvfg " y kj " vj g" qdugt xgf " hgttqo ci pgvkuo 0' Cnuq"cp"qr vko wo "f wpeg"y cu'tgs wktgf "vq" r tqf weg"gpqwi j "Vk<sup>5</sup>- " kpu" nggr kpi " vj g" et {ucnrkpg" qtf gkpi "kpcev"} \ j qw' gv' cr0' \*422; +\_0' Kp" ecug" qh'



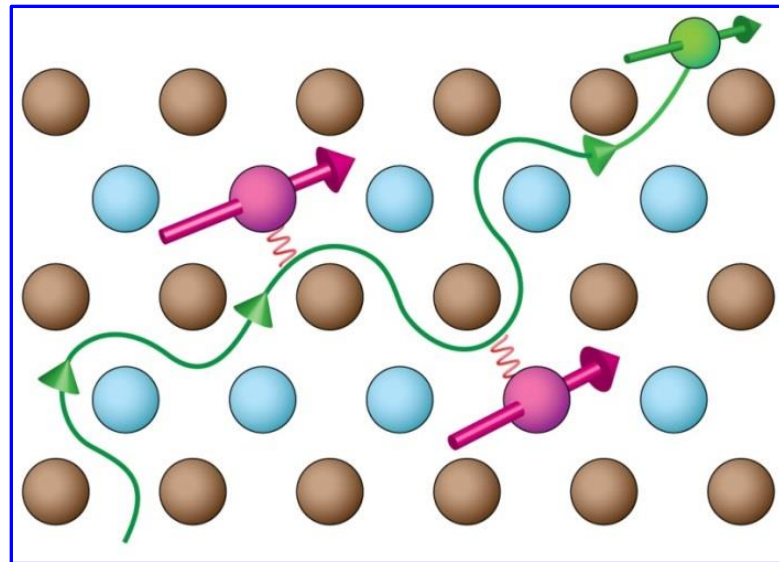
r qn{et { ucnkpg"twkn"vcti gv."ko r ncpvkvq lktcf kvkqp"qh"6"O gX"<sup>62</sup>Ct<sup>-7</sup> "kpu"cnq"  
kpf wegf "hgttqo ci pgvkuo "f wg"vq"qz {i gp"xcecepekgu"]Ucp{cn'gv'crl0\*4236+0J gpeg"  
wug" qh" kqp" dgco " ecwugu" eqpvqmgf " utwewtcl' f kuqtf gt" vj cv' o qf khgu" vj g"  
o ci pgvke"cu'y gm'cu'grgevtqple"r tqr gt vku0k"qvj gt "ugpug"qpg'o c{ "wug"kqp"dgco u"  
cu'c'r qvqpvkcn'vqql'ht'f ghgev'gpi kpggtkpi "kp"o cvgtkcn'uekgpeg0"

"

### 2.4 Discrepancies in Observed Ferromagnetism

Vj g" cdqyg" gzt gtko gpvcn' hkp kpi u" gzekg" dqvj " gzt gtko gpvcruu" cpf "  
vj gqgtvkekpu"vq"eqo r tgi gpf " vj g"rj gpqo gpc"qp"vj g"dcuku"qh"xctkqu"o qf gnu"  
\*f kuewugf "kp"Ej cr vgt"K0J qy gxgt."vj g"gzcev'qtki kp"qh'hgttqo ci pgvkuo "kp"vj gug"  
u{uvgo u'ku'vkn'eqo r ngz"cpf "wpenct0Hqt"gzco r ng."uco r ngu'r tqf wegf "kp"qz {i gp"  
tlej "cwo qur j gtg'uj qy "pgi rki kdr"o ci pgvkvkqp'uwi i gukpi "gzegu"qh'qz {i gp"cu"  
c'hcevqt"vj cv'f gytkqtcvgu"vj g"o ci pgvkuo "]Mko "gv'crl0\*4224+0'Mko "gv'crl0\*4227+ "  
cpf "Uj kpf g"gv'crl0\*4226+"pqvkegf "vj g"r t gugpeg"qh"Eq"enwvgtu"kp"vj gk"uco r ngu"  
ngcf kpi " vq" hgttqo ci pgvke" qtf gt" kvugcf " qh" kvtkpule" ecttkgtu" o gf kvkpi " vj g"  
o ci pgvkuo 0' Qp" vj g" qvj gt" j cpf." vj g" gzt gtko gpvcn' tguwu" qdvkpgf" d{ "  
Uwt {cpctc{cpcp"gv'crl0\*4227+"kp"Hg"cpf "Eq/f qr gf "VQ4"vj kp"hrk u"j ki j rki j vgf "  
vj g" ko r qtvcpv' tqrg" qh" qz {i gp" xcecepekgu" ftkkpi " vj g" tqgo " vgo r gtcwtg"  
hgttqo ci pgvkuo "kp"HgIEq'uvdurkwwgf "VQ4'hrk u0"

Tgegpv{."Qj uwnk'gv'crl0\*4233+'wukpi "vj g'uwthceg'cpf "dwm'ugpukkg'z/tc{ "  
rj qvqgo kuukqp" cpf "Z O E F " o gcuwtgo gpvu." gzt gtko gpvcn{ "f go qpvtcvgf " vj cv"  
hgttqo ci pgvkuo "ku"o gf kvvgf "d{ "Vk'5f" grgevtqpu" vj cv'eqwr ng" vj g"ur kpu"qh"Eq"  
cvqo u" hgttqo ci pgvkecn{ "cu" ungvj gf " kp" Hki 040" ]Qj uwnk' gv' crl0 \*4233+0' k"  
cf f kvkqp."vj g'ghgev'qh'grgevtke"hrf "kp"uy kej kpi "vj g"o ci pgvkvkqp"ku'ng{ "kuwg"  
hqt"ur kvtpkle"cr r rkevkvpu0'Tgegpv{." [ co cf c" gv' crl0 \*4233+ "uj qy gf "grgevtke"  
hrf" kpf wegf " tqgo " vgo r gtcwtg" hgttqo ci pgvkuo " kp" Eq/f qr gf " VQ4' D{ "  
cr r n{ kpi "c"i cvg"xqnci g"qh"chgy "xqnu."c"my /ecttkgt"r ctco ci pgvke"ucvg"y cu"  
vcpuhqto gf "kvq" c"j ki j /ecttkgt" hgttqo ci pgvke"ucvg"tgxgerkpi " vj g"uki pkkcpv"  
tqrg'qh'grgevtqpe'ecttkgtu'kp"vj gug"FO U'o cvgtkcn"] [ co cf c"gv'crl0\*4233+0'



**Fig.2.5** "C" tgr tgu pvcvkqp "qh" c" yj kp "hko "qh" Eq-VkQ<sub>4</sub> "kp" y j lej "hgttqo ci pgvkuo " ctkgu" dgecvug' vkcpkwo "5f "grgevtqpu" \*i tggp+vtcxgn'ctqwpf "vj g" o cvgtken'crki plpi " yj g'ur kp "qh" eqdcn'cvqo u" \*r kpm" uq" yj cv' yj g{ "cm' r qkp' kp" yj g' uco g' f kgevkqp0Vj g" dnwg" cpf "dtqy p" ur j gtgu" eqttgur ppf "vq" vkcpkwo "cpf "qz {i gp'cvqo u. 't gur gevkggn{0 ]Chgt "Qj wwnk'gv'cr0\*4233+\_"

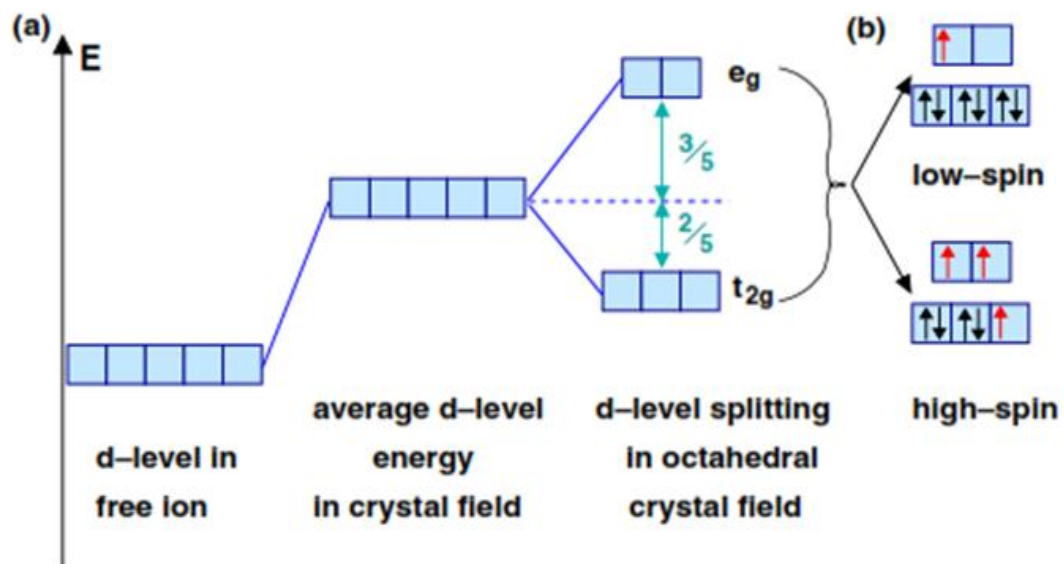
Vj qwi j " hgttqo ci pgvkuo " j cu" dggp" tgr qtvgf " d{ " xctkqu" y qtngtu." yj g" tgr tqf vekdkk{ "cpf "rcem'qh" wpls wpguu" qh" yj g" qdugt xgf " o ci pgvke" o qo gpv' j cu" r w' yj g" qtki kp" qh" o ci pgvkuo " uwr lekqu0Hqt" gzco r ng. "9cv0 "Eq/f qr gf "VkQ<sub>4</sub>" kp" cpcvcug" hqto "uj qy p" vq" j cxg" f hgtgpv" o ci pgvke" o qo gpv" rknq" 2054"  $\mu_B$  IEq" ]O cvwo cvq" gv' cr0' \*4223+\_" 3077"  $\mu_B$  IEq" ]Mko " gv' cr0' \*4225+\_" cpf "306"  $\mu_B$  IEq" ]Uj kpf g" gv' cr0' \*4225+\_0' Hqt" yj g" uco g" 9' "Eq/f qr gf "VkQ<sub>4</sub>" kp" twknq" hqto " yj g" o qo gpv' ku" tgr qtvgf " vq" dg" 3077"  $\mu_B$  IEq" ]J w' gv' cr0' \*422: +\_0' Kp" ecug" qh" pcpqr ctveng. "9cv0 "Eq/f qr gf "VkQ<sub>4</sub>" kp" cpcvcug" hqto "j cxg" uj qy p" c" f getgcugf " xcnwg" qh" o ci pgvke" o qo gpv. "Kq0" 208"  $\mu_B$  IEq" ]Rgtgkc" gv' cr0' \*422: +\_0'

Vj g" xctkqu" o ci pgvke" o qo gpv' qdugt xgf "kp" yj g" chqtgo gpvkppgf "tgr qt wu" uwi i guv' vq" wpf gtucpf "yj g" qz kf cvkqp" ucvg" qh" Eq" cv' VK' ukv0Vj g" qz kf cvkqp" ucvg" hqt" uwdukwkwqpcn' Eq" o wuv' dg" - 40J qy gxgt. "yj g" kqple" i tqwpf "ucvg" qh" Eq" ku" f gdcvfg 0Vj g" y q' r qukdkkkku" qh" Eq<sup>4</sup> "y kj " j ki j "ur kp" \*5f<sup>9</sup>. "U?" "5H+" ]Mko "gv' cr0' \*4225+\_" qt" nqy "ur kp" \*5f<sup>9</sup>. "U?" "3H+" ]Ej co dgtu" gv' cr0' \*4223+\_" ucvg" ku" qhngp' tckugf " \*uj qy p" kp" Hki 0' 408-0' Nqqnki " cv' yj g" y kf g" ur tgcf " qh" yj g" qdugt xgf " o ci pgvke" o qo gpv. "k' tgcml" o cnqu" k' vqwi j "vq" wpf gtucpf "yj g" gzcev' kqple" i tqwpf "ucvg" qh"

Eq<sup>0</sup>Vj g'htqo wrc'wugf "vq'ecrewrvg'yj g'ur kp/qpn{ "o ci pgvke"o qo gpv\* $\mu_{S.O}$ +ecp"dg" y tkwgp'cu'yj g'pwo dgt'qh'wpr cktgf "grgextqpu"-pø'cv'yj g'qwgto quv'qtdkcn'cu<

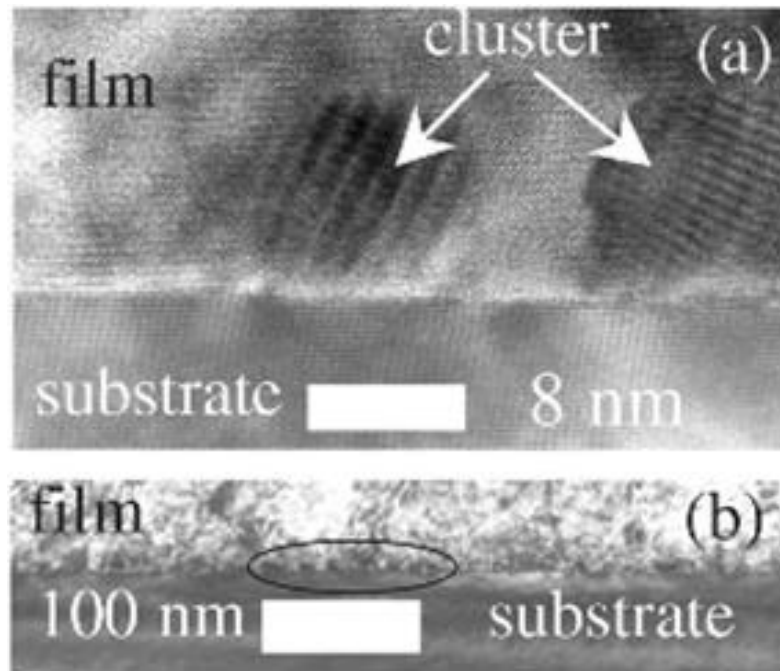
$$\mu_{S.O} \approx \sqrt{n(n+2)} \mu_B$$

Uq"o ci pgvke"o qo gpv'qh'Eq'kp"j ki j "cpf "mqy "ur kp'ucvgu'ctg"50 9" $\mu_B$ "cpf " 305" $\mu_B$ ."t gur ge'v'xgn{0J qy gxgt."yj gug'xcnvgu'ctg"r wtgn{ "hqt"o gvenke"Eq"cpf " o quv'qh'yj g'g'zr g'kø gpvcn'tguwmu"uj qy "o ci pgvke"o qo gpw'u'yj cv'ctg"rguu"yj cp" yj gug'yj g'q'g'v'kecm{ 'r tgf le'v'gf "xcnvgu"y j gp'Eq'ku'f qr gf 'kp'VkQ<sub>4</sub>0'



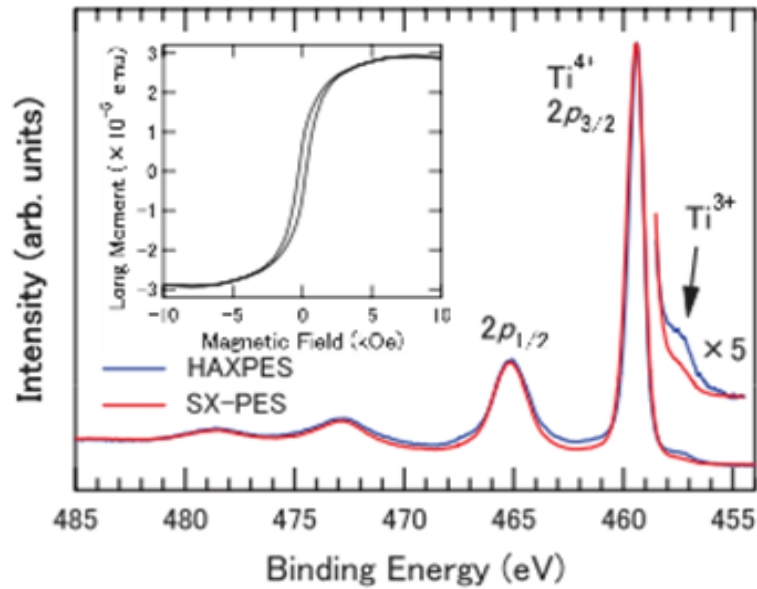
**Fig.2.6** "c+"Ur rkvkpi "qh'f "ngxgnu"kp"cp"qevcj gf tcn'et { ucn'Lgrf "cpf "d+r quukdrq" qeewr cvkqp"uej go gu'hqt"c"Eq<sup>4+</sup> \*5f<sup>9</sup>6u<sup>2</sup>+cvqo 0'Wpr cktgf "ur kpu'ctg"j ki j rki j vgf 0' ]Chgt'Lcppkuej "gv'cr0\*4227+\_"

Uj kpf g'gv'cr0\*4226+"uj qy gf "yj g'enwvgtkpi "qh'Eq"cvqo u'cv'yj g'uwdutcvg" cpf " hkr " kvgthceg" hqt" 4" cv " Eq/f qr gf " VkQ<sub>4</sub>" hkr " f gr qukvgf " qp" T/CnQ<sub>5</sub>" uwdutcvgu'd{ "RNF "vgej pls wg0'Vj g'enwvgtkpi "qh'Eq"y cu'engctn{ "uggp"d{ "etquu/ uge'v'qpcn'VGO 0'Hki 0'40" "c+"uj qy u'yj g'o ci p'k'gf "kø ci g'qh'yj g'kvgthceg'tgi kqp" cu' f go ctecvgf "kp" Hki 0' 40" \*d+0' Vj g' r t'gugpeg" qh' Eq" cv' yj g' d'v'm' y cu' cnuq" gxkf gpegf 'htqo "o ci pgvke"cpf "TDU"o gcuwtgo gpw'Uj kpf g'gv'cr0\*4226+0'



**Fig.2.7** VGO "ko ci g"qh"Vk<sub>20</sub>: Eq<sub>2024</sub>Q<sub>4</sub> "hko "cv"fhgtgpv"o ci plhkvkqp" ]Chgt" Uj kpf g"gv"cr0\*4226+\_"

Qj vwnk'gv'cr0\*4233+"uwf kcf "vj g"uwthceg"cpf "dwm'grgevtqple"r tqr gt vku" qh"Vk<sub>20</sub>Eq<sub>2027</sub>Q<sub>4</sub> "vj kphko u"fg r quksgf "d {"RNF "qp"Ut VkQ<sub>5</sub>"uwdutcvgu"wukpi "uqhv" cpf" j ctf " z/tc{" r j qvqgo kuukqp" ur gevqueqr {" wukpi " u{pej tqvtqp" tcf kvkqp" ]Qj vwnk'gv'cr0\*4233+0Vj g'hgttqo ci pgvkuo "kp"vj g"uco r ng'y cu'f gr kvgf "d {"vj g" j {uvgtguku"uj qy p"cu"kpugv"qh"Hki 040 "J ctf "z/tc {"RGU"cpf "uqhv"z/tc {"RGU"y gtg" o gcuwtgf "y kj "r j qvqp"gpgti kgu"qh"9; 62"cpf "3422"gX."tgur gevkggn(0Vj g"r tqdg" ugpukkxk{"hqt"uwthceg"y cu"3"po "cpf "c"32"po "hqt"dwm0Vj g"l qgo gf "xkgy "qh"vj g" Vk'4r<sub>54</sub>"ergctn{"uj qy u"vj g"Vk<sup>5-</sup> "eqo r qpgpv"r tgugpv"kp"vj g"dwm0ZCU"cpf "TRGU" j cxg" tngxcmf "Vk<sup>5-</sup> "grgevtqpu" cv" Hgto k' ngxgn' cpf " j ki j " ur kp" Eq<sup>4-</sup> " grgevtqpu" qeewtlkpi "cy c {"htqo "vj g"Hgto k'ngxgn0Cwj qtu"j cxg"uwi i guvgf "vj g"eqpf kvkqp"hqt" ej cti g" pgwtcrk{" i cxg" tkug" vq" vj g" gnwukxg" Vk' 5f" ecttkgtu" o gf kvkpi " hgttqo ci pgvkuo "xk"Eq"5f/Q"4r/Vk'5f" gzej cpi g"kpvtcevkvqp" ]Qj vwnk' gv' cr0 \*4233+0'



**Fig.2.8** XPS spectra of Ti 2p core level for Ti<sup>4+</sup> and Ti<sup>3+</sup> states. The inset shows the magnetic moment as a function of magnetic field.

Dgukf gu" fqr kpi ." k' j cu" dggp" uj qy p" vj cv' gzvtpuke" ghgeu" rknq" wplvpgvkvpcn'lpeqtr qtcvkqp"qh'o ci pgvke"ko r vt kkgu'f vt kpi "vj g"eqwtug"qh'uco r ng" j cpf r kpi "y kj "o gvcme" \*cu" eqpukf gtgf "pqp/o ci pgvke" uvckprguu"uvgnn" ur cwruc" cpf "hqtgr u'ecp"vtcpuhgt"o ci pgvke"ko r vt kkgu'qpvt"vj g'uco r ng"dghqtg"vj g'uco r ng" ku'o qwpvgf "hqt"US WKF"o gcuwtgo gpv'0'k'cf f kkkp."Vghrnp"vcr gu'qt"qyj gt'r rucvke" uwr r qtv'wugf "vq"o qwpv'vj g'uco r ngu'hqt"US WKF"o gcuwtgo gpv'o wuv'dg"gzco kpgf " vq" cuegtvckp" vj g" kvtpuke" hgttqo ci pgvke" r tqr gtv{ " qh" vj gug" F O U" u{uvgo u0' Uqo gvko gu"vj g"eqpvc"o kpcvkqpu"qh"vj g"cu"r wtej cugf "uwdutvcvu"cnq"i kxg"tkug"vq" hgttqo ci pgvko "kp"vj g'f gr qukvf "hko u"]Qi crg"\*4232+"Mj crkf "gv'ci0"\*4232+"[ gg" gv'ci0"\*4233+\_0'Gctrkgt "k'y cu'dgrkxgf "vj cv'qdugtxcvkqp"qh"CJ G"ku"c"t wg'hgcwtg" qh'kvtpuke" F O U" r tqr gtv{ "]Tco cpvk'gv'ci0"\*4229+\_0'J qy gxgt."Uj kpf g"gv'ci0' \*4226+"qdugt xgf "vj g"CJ G"kp"Eq/fqr gf "VkQ4"vj kp"hko u'f wg"vq"vj g'r t gugpeg"qh" Eq'emwvgtu0'

J gpeg."htqo "cm'vj gug"qdugtxcvkqpu"kv'ku"eqphko gf "vj cv'vj g"xcvng"qh"VE." O U."fqr cpv'uqrvdkkv{ "ctg'pqvtgr tqf wkdng0'cnq"vj gtg"ku"pq"ukpi ng"gzr gtko gpvcn" ej ctcevgtk vkqp"vej pks wg"ku"cxckrdng"vq"eqphko "vj g"kvtpuke" F O U" pcwtg0' J qy gxgt."qpg'ecp"qpn{ "vckrt"vj g'utwewtcn"o ci pgvke"qt"vtcpur qtv'r tqr gtvku0'

### 2.5 Objectives of the Present Thesis

Qy kpi "vq" vj g" ko r qtvcpv" tqrq" qh" f ghgeu" rknq" qz { i gp" xcecpkqu" kp" vj g" utwewtcn" grgevtke" cpf "o ci pgve" r tqr gt vku" qh" vj g" V<sub>k</sub>Q<sub>4</sub>. "kv" ku" kp vgt gukpi "vq" uwf { " ku" r tqr gt vku" d { " eqpvtkm kpi " vj g" f ghgev" eqpegpvtcvkp0' Vj g" qdlgevkxgu" qh" vj g" r tguv' vj guku" ctg<

- Vq"uwf { "vj g" cpcvcug" vq" twknq" vcpuhqto cvkqp" y kj "uk" g" tgf wegf "vq" pcpq" o gvgt" t cpi g. "y j gtg" vj g" f ghgev" eqpegpvtcvkqp" ku" uwr r qugf "vq" dg" xgt { "j ki j 0' Cnuq" hqewu" qp" vj g" o ci pgve" r tqr gt vku" qh" Eq" f qr gf "V<sub>k</sub>Q<sub>4</sub>" pcpqr ct vku" 0'
- Vq"uwf { "vj g" o ketquutwewtg" cpf "o ci pgve" r tqr gt vku" qh" V<sub>k</sub>Q<sub>4</sub>" pcpqy kt gu" u { p vj guk" gf "d { "j { f tqv j gto cn' vej pls wg0'
- Vq" hqewu" qp" vj g" ghgev" qh" qz { i gp" r ct vkn' r tguuwtg" qp" utwewtg" cpf " o ci pgve" r tqr gt vku" qh" V<sub>k</sub>Q<sub>4</sub>" cpf " Eq/ f qr gf " V<sub>k</sub>Q<sub>4</sub>" \*EVQ+" vj kp" hkn u" f gr qukvf "qp" Uk" cpf "NcCrQ<sub>5</sub>" uwdutcvgu0' Cu" vj g" o ci pgvkuo "kp" uvej "f qr gf " u { uvgo u' eqo gu" wpf gt "vj g" uecppgt" t gi ctf kpi "ku" kvtkpule" dgj cxkvw. " qpg" j cxg" vq" ectghwm { "g zr mqtg" vj g" qtki kp" qh" o ci pgvkuo "cxqkf kpi "cp { "uqtu" qh" ko r wkv { "eqpvtkdvwkp0'
- Vq" xcrlf cvg" vj g" wplxgtucrv { " qh" vj g" hgttqo ci pgvkuo "kp" pcpquutwewtgf " V<sub>k</sub>Q<sub>4</sub>" vj kp" hkn u" i tqy p" qp" Uk" uwdutcvg" d { "g/ dgco " gxcr qtcvkv" vej pls wg" y j lej "j cu" pqv' dggp" wugf "hqt" vj g" o ci pgve" uwf { . "y kj " uwdugs wgpv" r quv' cppgcnkpi "kp" qz kf k kpi "cu" y gni' cu' tgf wekpi "cvo qur j gtgu0'
- "Vq" o qf kh { "vj g" utwewtcn' cpf "o ci pgve" r tqr gt vku" qh" V<sub>k/z</sub>Eq<sub>z</sub>Q<sub>4/</sub> " hkn u" chvgt" f gr qukvkqp" y kj "vj g" j gr "qh" uy kn' j gcx { "kqp" ktcf kvkqp" xct { kpi "vj g" kqp" hnvgep0"
- Vq"uwf { "vj g" vcpur qtv" cpf "o ci pgvq/ vcpur qtv" r tqr gt vku" qh" V<sub>k/z</sub>Eq<sub>z</sub>Q<sub>4/</sub> " hkn u' chvgt" kqp" ktcf kvkqp0"

Vj g" tguwu" qh" vj g" r tguv' vj kpxguki cvkqu" ctg" f kuewuugf "kp" vj g" uwdugs wgpv" ej cr vgtu0'