The Review of Physical Chemistry of Japan Vol. 47 No. 2 (1977)

X-RAY EMISSION SPECTRA INDUCED BY ION-ATOM COLLISIONS II

Effects of Chemical Bonding and Multiple Ionization on X-Ray Spectra

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High resolution spectra of Be K X-ray in Be and BeO, B K X-ray in B and BN, O K X-ray in several oxides and L X-ray in Cr, Mn, Fe and Co produced by H (0.3–1.8 MeV), He (0.25–2.0 MeV), N (0.3–1.1 MeV), N(e 0.3–0.85 MeV) and Ar (0.3–1.8 MeV) ion bombardments were measured with a Bragg crystal spectrometer.

The resulting K_α diagram, satelltite and hypersatellite lines, and X-ray transition energy shifts show important influences of chemical bonding and projectile ions. When the targets of compounds are bombarded with heavy ions, these effects are found to be especially significant. Furthermore, in the K and L X-ray spectra for heavy ion bombardments, it is observed that the amount of additional inner-shell ionization is strongly dependent on the nuclear charge of the incident ions.

Introduction

Recently, X-ray emission spectra excited by fast heavy ion bombardment have been studied with a high resolution spectrometer. It has been revealed that multiple ionization states dominate the spectra and lead to new transitions including satellite and hypersatellite lines, as described in the previous paper[1].

Moreover, several investigations of chemical effects on ion-excited X-ray spectra have been reported. It is well known that X-ray spectra are sensitive to the chemical bonding of the emitting atom and of great use for the study of the atomic and electronic structure in materials[2]. The binding energy of the inner-shell is large, whereas that of the valence shell is small, so the X-ray transition between the inner-shells in molecules or compounds suffer only a small perturbation and is changed slightly in energy or intensity. On the other hand, very large chemical energy shifts have been observed if the electrons involved in the X-ray transition come from the valence shell. This is understood from the measurements of Al K X-rays in Al and Al_2O_3[3] and Si K X-rays in Si and SiO_2[4] where the inner-shell transitions, K_α diagram and satellite lines, exhibit smaller difference than the valence shell transitions, K_β diagram and satellite lines. Furthermore, the drastic effects of

(*Received September 25, 1977*)

1) K. Kawatsura, *This Journal*, 47, 53 (1977)
2) D. J. Nagel and W. L. Baun, X-Ray Spectroscopy, edited by L. V. Azároff, p. 445, McGraw Hill, New York (1974)
3) P. G. Burkhalter, A. R. Knudson, D. J. Nagel and K. L. Dunning, *Phys. Rev.*, A6, 2093 (1972)
4) J. McWherter, D. K. Olsen, H. H. Wolter and C. F. Moore, *Phys. Rev.*, A10, 200 (1974)

chemical bonding are presented by the measurements of the K X-ray spectra from the Be atom in Be and BeO[5], from the B atom in B and BN[6] and from the F atom in several fluorides[7], where the K_α diagram lines involve the electronic transitions coming from the valence shell.

In the present work, we report an extensive investigation of the K X-ray spectra from Be, B and O atoms and the L X-ray spectra from Cr, Mn, Fe and Co atoms produced by H^+, He^+, N^+, Ne^+, Ar^+ and Ar^{2+} ions in the energy range of 0.25 to 2.0 MeV. Discussions are also given concerning the effects of chemical bonding on the spectra of Be K X-rays in Be and BeO, and B K X-rays in B and BN, and the multiple inner-shell vacancy production in the K X-ray spectra from Be, B and O atoms in the same targets and the L X-ray spectra of Cr, Mn, Fe and Co metal targets. Measurements of the K and L X-ray spectra with a high resolution spectrometer have been performed on a number of the thick solid targets using the ion beams from a 2-MV Van de Graaff accelerator.

Experimentals

The experiments were carried out by the use of the ion beams from a 2-MV Van de Graaff accelerator of Japan Atomic Energy Research Institute. A vacuum Bragg crystal spectrometer was used for obtaining the X-ray emission spectra produced by H^+, He^+, N^+, Ne^+, Ar^+ and Ar^{2+} ion bombardments on the thick targets. The doubly charged Ar^{2+} ions were sometimes employed to extend the incident energy range. The measurements of the K X-ray spectra from Be atoms were performed with a pseudo-crystal of the lead-lignocerate soap film with 100 layers (*2d* spacing=130 Å). The measurements of the K X-ray spectra from B atoms were performed with a pseudo-crystal of the lead-stearate soap film with 100 layers (*2d* spacing=100 Å). The measurements of the K X-ray spectra from O atoms and the L X-ray spectra from Cr, Mn, Fe and Co atoms were performed with a single crystal of rubidium hydrogen phthalate (*2d* spacing=26.1 Å). This device was the same as that mentioned in the previous paper[1].

Results and Discussions

Be K X-ray spectra of Be and BeO

The effects of chemical bonding on the Be K X-ray spectra induced by 0.3 MeV H^+, 1.2 MeV He^+, 1.1 MeV N^+ and 0.45 MeV Ar^+ ion bombardments are illustrated in Fig. 1[5]. In the spectra for the Be target, K_α diagram line appears at 108.5 eV, whereas K_α^2 hypersatellite line corresponding to the transition from K^{-2} initial to $K^{-1}L^{-1}$ final vacant state at 146.1 eV except for the H ion case. However, the latter line was previously observed in the H ion case as well as the He ion,

5) K. Kawatsura, K. Ozawa, F. Fujimoto and M. Terasawa, *Phys. Lett.*, **A60**, 327 (1977)
6) K. Ozawa, K. Kawatsura, F. Fujimoto and M. Terasawa, *Nucl. Instrum. Methods*, **132**, 517 (1976)
7) C. F. Moore, D. L. Matthews and H. H. Wolter, *Phys. Lett.*, **A54**, 407 (1975)

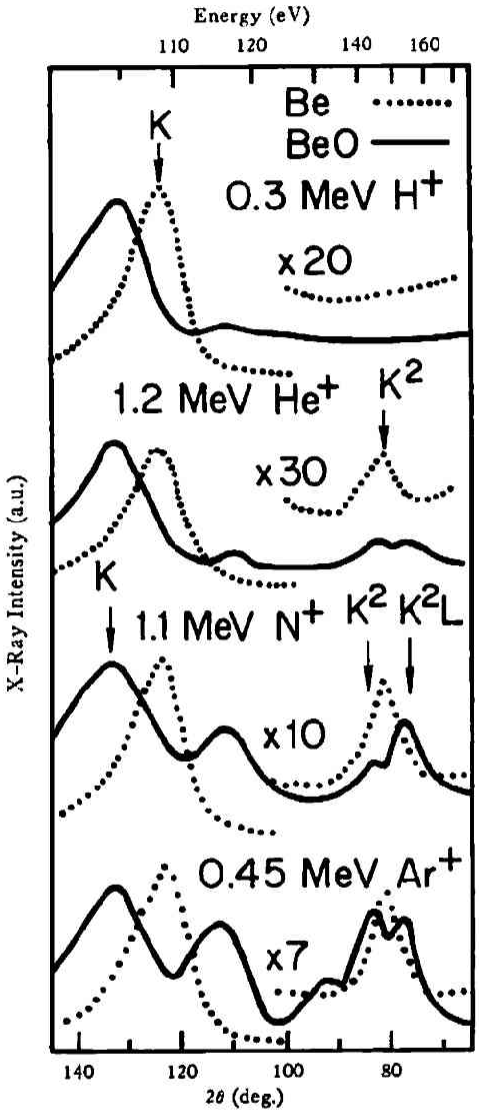

Fig. 1 K X-ray spectra of Be from the thick Be (dashed curve) and BeO (solid curve) targets induced by 0.3 MeV H^+, 1.2 MeV He^+, 1.1 MeV N^+ and 0.45 MeV Ar^+ ion bombardment.

using the step scanning method[8]. The atomic energy levels for the Be atom were calculated with the nonrelativistic Hartree-Fock-Slater (HFS) program of Herman and Skillman[9]. The result shows the values of 110.1 and 140.4 eV forthe K_α diagram and K_α^2 hypersatellite X-ray transitions, respectively. With increasing nuclear charge of the incident projectile, the intensity of the K_α^2 hypersatellite lines is enhanced. The inner-shell ionization in the Be atom is described by the direct

8) K. Kawatsura, K. Ozawa, F. Fujimoto and M. Terasawa, *Proc. 10th Int. Conf. on Physics of Electronic and Atomic Collisions, (Paris) Abstracts* p. 50, (1977) and to be published in *Phys. Lett. A*

9) F. Herman and S. Skillman, "Atomic Structure Calculations", Prentice Hall, Englewood Cliffs, New Jersey (1963)

Table 1. X-ray energies and chemical shifts in eV for K X-ray spectra by 1.1 MeV N^+ ion bombardment with the calculated values

Initial vacancies	X-Ray transition	X-Ray energy Be	(HFS)	BeO	Energy shifts
K	Be (L)→Be (K^{-1})	108.5	(110.1)	104.4	−4.1
KL	O (L)→Be ($K^{-1}L^{-1}$)			116.0	
K^2	Be (L)→Be (K^{-2})	146.1	(140.4)	142.3	−3.8
K^2L	O (L)→Be ($K^{-2}L^{-1}$)			153.8	

Coulomb excitation for light ion bombardment[1,10,11]. On the other hand, for heavy ion bombardments with N or Ar ion[11], the inner-shell ionization caused by the electron promotion mechanism is shown.

For the BeO target, the spectra become more complicated. Namely, both the K_α diagram and K_α^2 hypersatellite lines become broader and shift to lower energy and then new satellite lines appear in higher energy side of each main peak. Table 1 summarizes the X-ray energies and the chemical shifts in energy for Be and BeO induced by 1.1 MeV N^+ ion bombardment. In this table, the computed X-ray transition energies for the Be atom are also listed using the HFS approximation[9]. According to the observation of X-ray photoelectron spectroscopy, Hamrin *et al.*[12] have shown that the Be 1s level shifts about 2.8 eV toward a higher binding energy as metal was converted into oxide. The chemical energy shift in the Be X-ray emission spectra from Be and BeO excited by X-ray or electron and the existence of a faint satellite line at about 11.6 eV higher than the K_α diagram line are seen in the literatures[13,14]. They did not explain where the satellite line came from. Our results of X-ray energy shifts of −4.1 eV for K_α diagram and −3.8 eV for K_α^2 hypersatellite lines are in a good agreement with the results for the electron bombardment[14]. The above negative energy shifts seem reasonable according to the fact that the change in the valence shell energy is about 4 eV larger than that in the core-level binding energy[12,14]. The widths of the Be K X-ray emission band for Be and BeO are about 11.5 eV and 10.5 eV, respectively. This gives the width of the filled part of the valence shell reflecting the density of states.

In addition to the above main lines, the K_α satellite and hypersatellite lines were observed at 116.0 eV and 153.8 eV, respectively. These were found in all the spectra except the hypersatellite line for the H ion bombardment. In the case of Ar ion bombardment, the quantitative analysis of the X-ray lines was difficult because of overlapping with the second order lines of the Ar L X-rays. The respective intensity ratios of the satellite or the hypersatellite peaks to their main peaks increased with increasing projectile nuclear charge. With the N ion bombardment, it seems that the intensity of the KL line is lower than that of the K line while the intensity of the K^2L line is

10) F. Fujimoto, K. Kawatsura, K. Ozawa and M. Terasawa, *Phys. Lett.*, **A57**, 263 (1976)
11) M. Terasawa, *J. Phys. Soc. Japan*, **33**, 1420 (1972)
12) K. Hamrin, G. Johansson, U. Gelius, C. Nordling and K. Siegbahn, *Physica Scsipta*, **1**, 277 (1970)
13) R. C. Ehlert and R. A. Mattson, *Advances in X-Ray Analysis*, **9**, 456 (1966)
14) A. P. Lukirskii and I. A. Brytov, *Sov. Phys.-Solid State*, **6**, 33 (1964)

higher than that of the K^2 line. This fact can be understood by considering that the absorption edge of BeO lies at about 118 eV above the K_α satellite region. The new satellite lines enhanced are explained by the increase of multiple ionization in L-shell by heavy ion bombardments. In this case, this increase corresponds to the production of the vacancies in the valence shell. The 11.6 eV energy separation between K and KL lines is very similar to 11.5 eV separation between K^2 and K^2L lines. On the other hand, the charge transfer from the Be atom to the O atom through the chemical bonding is 1.3 electrons according to Pauling[15]. This indicates that the valence electrons in BeO are mainly localized near the O nucleus. The HFS calculations have shown that the K-shell binding energy of the Be atom increases about 11.5 eV when an electron in L-shell is removed off. This energy shift is coincident with both the measured energy separations between K and KL, and between K^2 and K^2L lines. Since heavy ion-atom collision may enhance the multiple ionization in the inner- and outer-shell, it can be concluded that the electrons involved in the KL and K^2L transitions in BeO come from the valence shell in the O atoms, as summarized in Table 1.

B K X-ray spectra of B and BN

Fig. 2 shows the X-ray spectra of B and BN induced by 0.7 MeV N^+ ion bombardment[6]. In the spectrum of the B target, K_α diagram and K_α^2 hypersatellite lines were observed at 183.7 eV and 232.4 eV respectively. These results were already discussed in the previous paper[1]. The spectrum of the BN target is much more complicated than that of the B target. The K_α diagram line has two satellite peaks in both energy sides of K_α line. The satellite peak in the lower energy side is denoted as K_0, whereas that in the higher energy side as KL. These three peaks were also observed in the cases of electron or light ion bombardments[13,16], however KL is much more faint compared to that of the present study. Moreover, their relative peak heights differ considerably from the present spectrum. On the other hand, K_α^2 hypersatellite line has only a satellite peak in the high energy side (K^2L). Furthermore, K_α diagram line of the N atom appeared at about 400 eV.

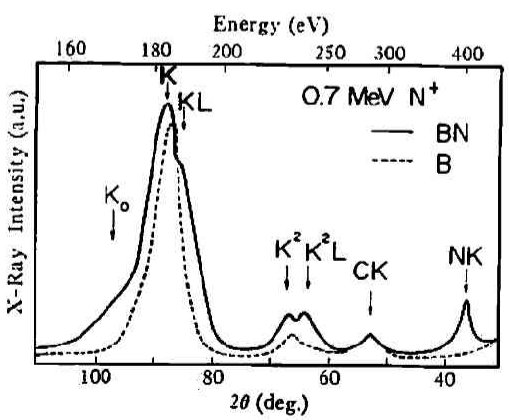

Fig. 2 K X-ray spectra from B and BN target induced by 0.7 MeV N^+ ion bombardment.

15) L. Pauling, "The Nature of the Chemical Bond", 2nd ed., Cornell Univ. Press, New York (1945)
16) K. Kawatsura, K. Ozawa, F. Fujimoto and M. Terasawa, "Ion Beam Surface Layer Analysis", edited by O. Meyer, G. Linker, F. Käppeler, Vol. 2, p. 719, Plenum Press, New York (1976)

Table 2. X-ray energies and chemical shifts in eV for K X-ray spectra by 1.1 MeV N^+ ion bombardment with the calculated values.

Initial vacancies	X-Ray transition	X-Ray energy B	(HFS)	BN	Energy shifts
K_0 (K)	N (2s)→B ($1s^{-1}$)			167.0	
K	B (2p)→B ($1s^{-1}$)	183.7	(188.8)	181.7	−2.0
KL	N (2p)→B ($1s^{-1}2p^{-1}$)			189.1	
K^2	B (2p)→B ($1s^{-2}$)	232.4	(225.3)	229.3	−3.1
K^2L	N (2p)→B ($1s^{-2}2p^{-1}$)			241.2	

Table 2 contains the X-ray energies and the chemical shifts in energy, for B and BN induced by 1.1 MeV N^+ ion bombardment. These values were obtained by the deconvolution of the spectra with consideration about the spectral profile from the B target. The Table contains also the results for the Be atom obtained by the HFS program for comparison. It was shown that the energies of the K_0, K and KL X-ray lines agree with those observed by electron bombardment[13].

Fig. 3 shows the X-ray spectra of BN induced by 0.3 or 1.1 MeV N^+ ion bombardment as well as the spectrum by 1.5 MeV H^+ ion bombardment. The profile of the spectrum and relative intensity of each X-ray line for the H ion bombardment are very similar to those caused by the electron bombardment. The very similar result was also obtained for the He ion bombardment. Here, it is found that the widths of the X-ray lines for heavy ion bombardment are broader than those for light ions. It should be noted that at low energy of the incident ions the intensity of the high energy satellites, KL and K^2L, is higher than that of the main peaks, K and K^2, respectively.

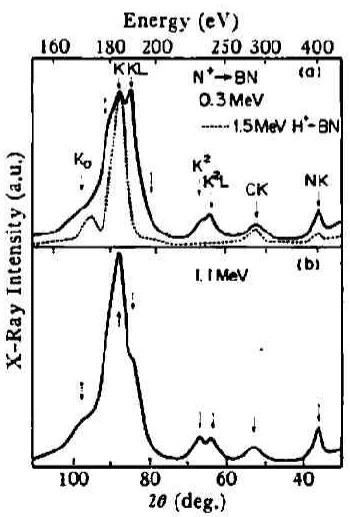

Fig. 3 (a) K X-ray spectra from BN induced by 1.5 MeV H^+ and 0.3 MeV N^+ ion bombardment: (b) by 1.1 MeV N^+ ion bombardent.

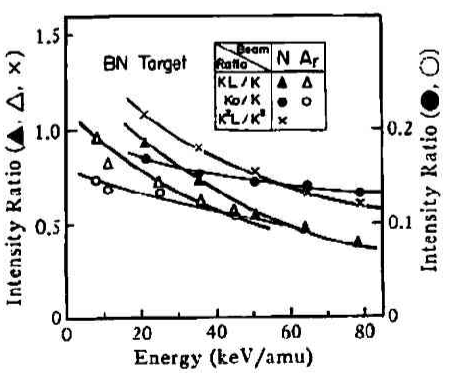

Fig. 4 The energy dependence of intensity ratio of each line from the BN target induced by N and Ar ion bombardment. For Ar ion, the quantitative analysis of K^2 and K^2L lines is difficult because of overlapping with Ar L X-rays.

In the case of the B target bombarded with Ar ion, the spectra observed were very similar to those bombarded with N ion except for the appearance of L X-rays of the Ar atoms. K_σ^2 hyper-satellite line due to initial double K-shell vacancy was also observed.

In the case of the BN target, similar spectra to those with N ion were observed, and relatively high intensity KL and K^2L lines were obtained. However, the K^2 and K^2L X-ray lines overlapped with the Ar L X-ray lines so that the quantitative analysis of these lines was rather difficult.

Fig. 4 shows the energy dependence of the peak height ratio of each line from the BN target. The intensity ratios of KL to K and K^2L to K^2 lines decrease noticeably with increasing incident energy of the N and Ar ions. The ratio of K_0 to K decreases also with increasing energy. But the energy dependence of the ratio is not so strong as is found in the other cases.

The variation of the KL intensity with the incident energy gives the same tendency as that of K^2L (Fig. 4). Probably K^2L line correlates with the double vacancies of the K-shell. The 2s vacancy state cannot remain stable because it should be filled up immediately through the Coster-Kronig process. Both KL and K^2L may be related to the initial 2p vacancy, since these appear in the high energy sides of the K and K^2, respectively. The B atom has only one electron in the 2p level. And 2p electrons of B and N atoms make a π-orbital. Therefore it can be concluded that the KL and K^2L X-ray lines come from the transitions from the 2p level of the N atom in BN to the 1s level of the B atom with the initial vacant states $1s^{-1}2p^{-1}$ and $1s^{-2}2p^{-1}$, respectively. There occurs the promotion of B 2s and 2p electrons through the level crossing of molecular orbitals temporarily formed during the collisions. It may contribute to enhance the 2p vacancy in the region of low incident energy. In electron and H ion bombardment, a faint peak of KL is observed though its origin is not clear. Here it can be also presumed that this is caused by the KL transition in BN, because it has become clear that electron or H ion bombardment removes multiple electrons simultaneously from K- and L-shell at low possibilities.

The intensity of the X-ray lines other than KL and K^2L increases rapidly with increasing incident energy. This can be explained again by the promotion mechanism for 1s electrons of the B and N atoms.

The intensity of the KL and K^2L X-ray lines increases slowly with increasing incident energy. This might be due to the difference of the electron promotion mechanism between K- and L-shell.

Considerations of the energy scheme of the B and N atoms lead to the conclusion that the other satellite K_0 line is caused by the cross-over transition from the electron of the σ-orbital to the 1s state of the B atom. It is likely that other faint satellites exist in the vicinity of 175 and 195 eV. These satellites are also observed by other authors[13]. However, the origin of these satellites has not yet been elucidated.

O K X-ray spectra of BeO

Fig. 5 shows the K X-ray spectra of the O atom emitted from BeO induced by 1.5 MeV H^+, 1.5 MeV He^+, 1.1 MeV N^+ and 1.8 MeV Ar^{2+} ion bombardments[17]. Similar spectra were found for

17) K. Kawatsura, K. Ozawa, F. Fujimoto and M. Terasawa, *Phys. Lett.*, **A58**, 446 (1976)

the targets of Li_2O, B_2O_3, MgO, Al_2O_3 and SiO_2 when they are bombarded with the charged particles. The K_α diagram line appears at 525 eV in each spectrum. The satellite peak for this line can be observed at about 532 eV in every spectrum. The intensity ratios of the satellite to the diagram line increase noticeably with increasing projectile nuclear charge. This may be ascribed to the increase of multiple L-shell ionization by heavy ion bombardments. Here, the ionization of this sort implies the production of multiple electron vacancies in valence shell.

The energy separation of these two peaks is about 7 eV. The heavy ion bombardment enhances

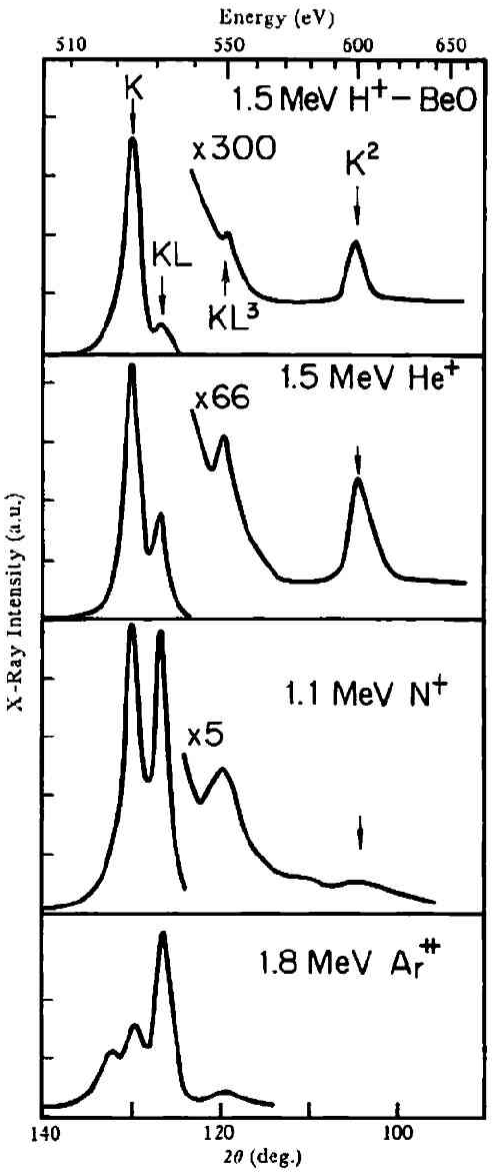

Fig. 5 K X-ray spectra of O from BeO induced by 1.5 MeV H^+, 1.5 MeV He^+, 1.1 MeV N^+ and 1.8 MeV Ar^{2+} ion bombardment.

the intensity of the satellite peak. From these facts the satellite peak can be assigned to the KL transition from the O atoms with single K- and single L-shell vacancies. It is worthy to note that absorption edges (~540 eV) for the oxides lie above the K_α satellite peaks. Consequently, it is difficult to assign other satellite peaks definitely. From energy considerations, however, another satellite peak at 550 eV also seems to come from the KL^3 transition of the O atoms.

A clear peak is observed at 600 eV for H ion, at 602 eV for He ion and 605 eV for N ion bombardment, respectively. (For Ar ion bombardment, the beam current was too weak to detect this line.) Apparently this line looks like a band. The width of this band varies remarkably with the incident projectiles. For H ion bombardment, it is narrow and becomes broader in He ion bombardment. It is very broad for N ion bombardment. These facts are considered to be due to the simultaneous K- and L-shell ionization, as already seen in the case of the K_α satellite lines. Then, the peak at 600 eV for H ion bombardment can be also assigned to K_α^2 hypersatellite transition from the O atoms with double K-shell vacancies. For heavy ion bombardments, the hypersatellite X-ray lines should include the K^2L^n transitions as well as K^2 transition. However, these lines cannot be resolved, because the accumulated counts of the X-rays are very low and the line broadening occurs during slow heavy ion-atom collisions in solids.

L X-ray spectra of 3d transition elements

Finally, the preliminary results of the L X-ray spectra by heavy ion bombardments are given[18].

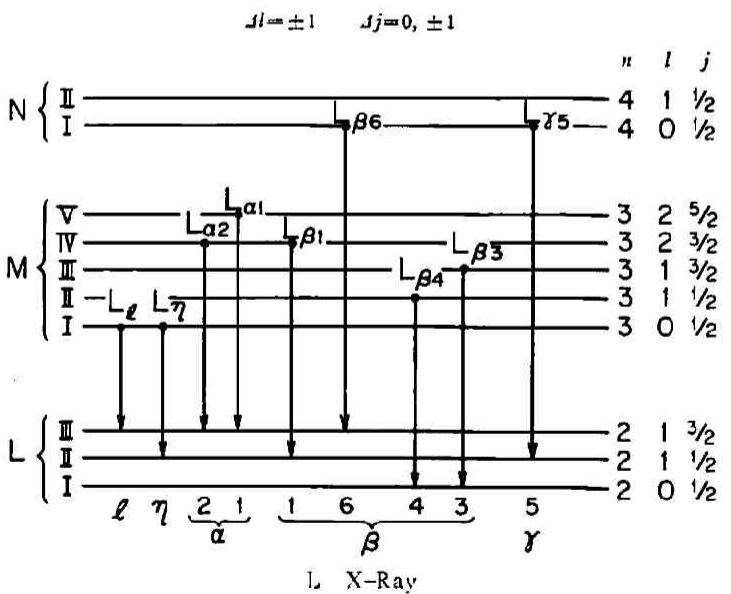

Fig. 6 Spectroscopic diagram for the major radiative transitions that comprise the characteristic L X-ray spectrum of the 3d transition elements.

18) K. Ozawa, K. Kawatsura, F. Fujimoto, K. Komaki and M. Terasawa, *Proc. 7th Int. Conf. on Atomic Collisions in Solids*, Moscow, Sept. 1977 (to be published)

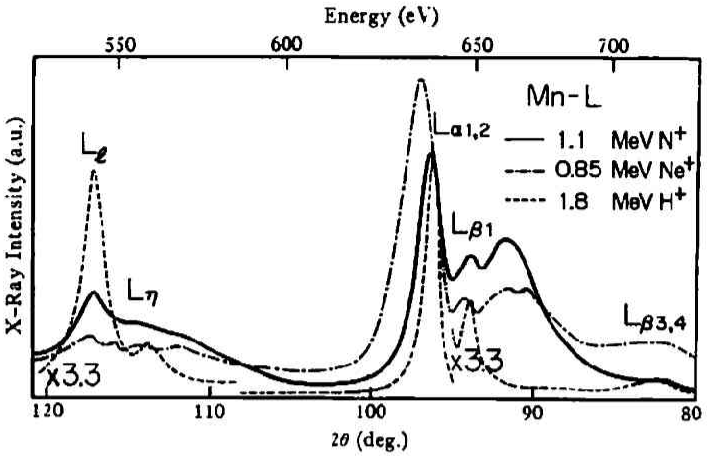

Fig. 7 L X-ray spectra of Mn induced by 1.8 MeV H^+, 1.1 MeV N^+ and 0.85 MeV Ne^+ ion bombardment.

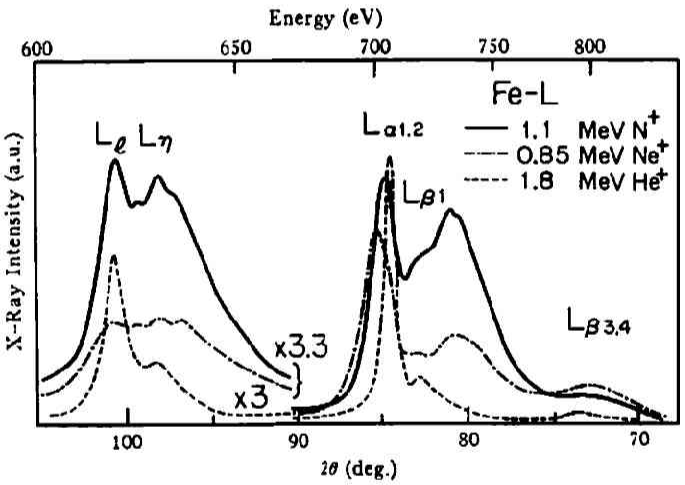

Fig. 8 L X-ray spectra of Fe induced by 1.8 MeV He^+, 1.1 MeV N^+ and 0.85 MeV Ne^+ ion bombardment.

A schematic diagram for major L X-ray transitions is shown in Fig. 6. Fig. 7 shows the L X-ray spectra of the Mn metal target induced by 1.8 MeV H^+, 1.1 MeV N^+ and 0.85 MeV Ne^+ ion bombardment. Fig. 8 shows the L X-ray spectra of the Fe target induced by 1.8 MeV He^+, 1.1 MeV N^+ and 0.85 MeV Ne^+ ion bombardments. The spectra from Cr and Co induced by heavy ion bombardments were also similar to those from the Mn and Fe targets. Broad satellite bands have been observed in the high energy sides of L_ℓ, L_η, $L_{\alpha_{1,2}}$ and $L_{\beta_{3,4}}$ peaks for the heavy ion bombardments. They are considered to arise from the multiple vacancies in the M- and N-shell during the heavy ion-atom collisions[19]. In this case, the L hypersatellites due to L-shell multiple vacancies are possible, cor-

19) P. G. Burkhalter, A. R. Knudson and D. J. Nagel, *Phys. Rev.*, A7, 1936 (1973)

responding to the K hypersatellites in the heavy ion collisions. However, contributions of the L hypersatellite X-rays due to the double L-shell vacancies are supposed to be superposed on the $L_{\beta_{3,4}}$ diagram and satellite lines.

The $L_{\alpha_{1,2}}$ peaks observed in the heavy ion bombardments apparently shift to the low energy side. Originally empty levels in the N-shell may be occupied by electrons promoted from inner-shells through the quasi-molecular orbitals, resulting in the inner-shell energy level shift. The shift of the 3d-subshell is considered to be the most signiñcant and its magnitude is expected to be a few electron volts. The perturbed $L_{\alpha_{1,2}}$ X-rays may contribute to the low energy part of the observed peak. This conclusion coincides with the fact that no shift is observed in the L_ℓ and L_η X-rays.

Acknowledgment

The author is grateful to Prof. J. Osugi for his interest and helpful advices in this work and for critical reading the manuscript. The author is indebted to Dr. K. Ozawa, Prof. F. Fujimoto, Dr. M. Terasawa and Dr. K. Komaki for their valuable suggestions and discussions throughout this work, and to Dr. S. Tsujimura and Dr. K. Izui for their continuous interest. The author also wishes to thank Mr. C. Kobayashi and Mr. S. Kanda for their kind operation of the 2-MV Van de Graaff accelerator.

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