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Photoabsorption of Ba $4d \rightarrow 4f$ in some solid barium compounds

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High-resolution photoabsorption spectra of Ba $4d \rightarrow 4f$ in the solids of barium compounds of BaO, BaS, BaF_2, $BaCl_2$, BaI_2, and $BaCO_3$ have been measured by using synchrotron radiation. The two distinguished photoabsorption lines observed in this work in the energy range of $92 \sim 97$ eV are identified to be atomlike spectra of barium arising, respectively, from the transitions of $4d^{10}\,{}^1S_0$ to $4d^9 4f^1\,{}^3P_1$ and $4d^9 4f^1\,{}^3D_1$. The line shapes and the peak energies of the photoabsorption lines from $4d^{10}\,{}^1S_0 \rightarrow 4d^9 4f^1\,{}^3D_1$ of these compounds have been determined by a curve-fit analysis. Below the resonance peak, some satellites are found in the solids of BaF_2, and $BaCl_2$. No such satellites can be identified in the other solids. The variation of the peak energies of the halides can be attributed mostly to the variation of the coordination charge of Ba ions as calculated by a simple formula, but it is not so for the oxides. [S0163-1829(99)02135-9]

I. INTRODUCTION

The photoabsorption of Ba $4d \rightarrow 4f$ has been an interesting subject in the atomic theory. The removal of an inner shell electron increases the central field sufficiently for $4f$ collapse to occur in the $4d^9 4f 6s^2$ configuration. Consequently two $4d^9 4f 6s^2$ levels accessible from the ground states, ${}^3D_1$ and ${}^3P_1$, become bound states of the inner potential well for f electrons and give rise to two quite strong absorption lines. The two lines are identified in barium vapor[1,2] as well as in barium metal.[3] Since the final states are localized in the barium core and are little affected by the metallic environment, the global feature of these two lines are similar to each other for the Ba vapor and the Ba metal.[2] This similarity has been shown to be a common feature for all lanthanide atoms and solids[4] as well. Due to the same reason, one expects that this similarity should extend to the solids of barium compounds. We shall show that it is indeed the case, they are very much atomlike in character.

Nevertheless, the contribution of Ba $5d$ electrons to the valence electronic structure in barium compounds may have some effects on the two spectral lines. The observed negative chemical shift of the core level of barium compounds was attributed to the increase occupation of Ba $5d$ states in the compounds.[5] The depression of superconductivity in $PrBa_2Cu_3O_{7-\delta}$ was also suggested to be caused by the localization character of Ba $5d$ states in the valence band based on the binding energy change of the core levels of Ba $3d$ and Ba $4d$.[6] In other words, the less occupation of Ba $5d$ states in $PrBa_2Cu_3O_{7-\delta}$ than in $YBa_2Cu_3O_{7-\delta}$ was proposed to localize the holes at the Ba site and consequently to the detriment of the superconductivity of $PrBa_2Cu_3O_{7-\delta}$.

In this report, we shall show the shape and the peak energy of the spectral line for the transition of Ba $4d^{10}\,{}^1S_0 \rightarrow 4d^9 4f\,{}^3D_1$ in some solids of barium compounds. The variation of the peak energies of the halides can be attributed mostly to the variation of the coordination charge of Ba ions as calculated by a simple formula, but it is not so for the oxides. The influence of the Ba $5d$ electrons in the oxides will be discussed.[7]

II. EXPERIMENT

The powders of BaO, BaS, BaF_2, $BaCl_2$, BaI_2, and $BaCO_3$ are commercially available. Their purities are greater than 99.99%. We find no degradation of the samples during the experimental runs for any fresh examples, even though the BaI_2 is moisture sensitive.

The Ba $4d$ photoabsorption spectra are measured using synchrotron radiation from the low-energy spherical grating monochromator beam line at the Synchrotron Radiation Research Center (SRRC), Taiwan, R. O. C. The energy resolution of the monochromator is set to be about 50 meV in that a 900-grooves/mm grating with slit openings of 100 μm is used. The total x-ray fluorescence yields of the sample, induced by synchrotron radiation, are recorded by a microchannel plate (MCP) which is operated at the bias voltage of 2 KV in the current mode. A nickel mesh with positive potential of 300 V relative to the sample was put near the sample to prevent ions from entering the MCP. The electrons are suppressed due to $\cong 2$ KV negative potential between the MCP and the sample. Both the surface normals of the target and the MCP are oriented 45° to the incident photon beams in which the MCP faces directly the irradiated face of the target. The probing depth of the incident photons is estimated from the x-ray attenuation data[8] to be around 100 Å.

The energy of the monochromator is calibrated by setting the energy of the most prominent Al L x-ray absorption peak

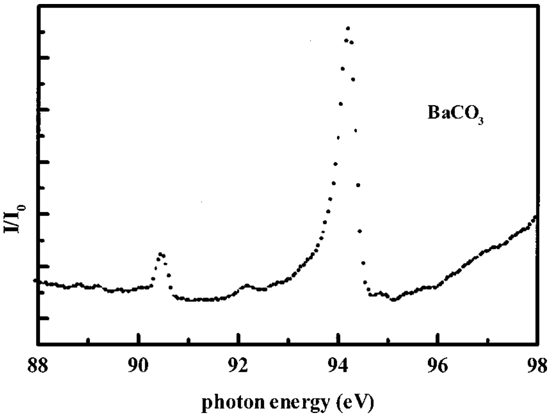

FIG. 1. The typical photoabsorption spectrum of Ba $4d$ edge of BaCO$_3$ in the energy range of 88 to 98 eV.

of α-Al$_2$O$_3$ at 78.80 eV.[9] The Ba $4d$ photoabsorption spectra are recorded mainly in the energy range of 92 to 97 eV by a fine scan step of 0.025 eV. Several experimental runs for each sample have been performed and the repetition is great except the energy shift of the spectrum caused by each electron injection of the machine, which can be nicely corrected by referring to the Al L x-ray absorption line aforementioned. The final spectrum is the sum of all these experimental runs. In a quick scan in the energy range of 88 to 98 eV one can observe two relatively narrow peaks (width$\cong$400 meV). The typical spectrum of BaCO$_3$ is shown in Fig. 1. Their energies are, respectively, 90.5 and 94.2 eV, separated by 3.7 eV. Their spectral shape is asymmetric. The spectral intensity ratio of the high-energy peak to the low-energy peak is roughly 10:1.

III. RESULTS AND DISCUSSIONS

As shown in Fig. 1, the energies of the two distinguished Ba $4d$ photoabsorption peaks of barium compounds are respectively to be about 90.5 and 94.2 eV, about 1.5 eV higher than the binding energies of $4d_{5/2}$ (89.9 eV) and $4d_{3/2}$ (92.6 eV).[10] The energy separation (3.7 eV) is also higher than that (2.7 eV) of $4d_{5/2}$ and $4d_{3/2}$. Apparently these two peaks cannot be properly described to be the transitions from the two spin-orbital splitting states of Ba $4d$. In fact they had been detected in barium vapor among other spectral lines[1,2] and interpreted to be the transitions of Ba from $4d^{10} \rightarrow 4d^9 4f^1$ due to the $4f$ collapse, similar to the $4d$ photoabsorption of La^{3+}. The $4d$ photoabsorption spectra of La^{3+} are ascribed by Sugar[11] to be the transitions of high-purity levels of $4d^{10}\,{}^1S_0$ to $4d^9 4f^1\,{}^3P_1$ and $4d^9 4f^1\,{}^3D_1$ having a slight admixture of $4d^9 4f^1\,{}^1P_1$. The levels of ${}^3P_1$, ${}^3D_1$, and ${}^1P_1$ are the multiplet levels of $4d^9 4f^1$ due to a considerable overlapping of the $4d$ wave function and the $4f$ wave function. The transition from $4d^{10}\,{}^1S_0$ to $4d^9 4f^1\,{}^1P_1$ is in fact the dominant transition which is about 2500 times larger than that of $4d^{10}\,{}^1S_0$ to $4d^9 4f^1\,{}^3P_1$ for Ba. It is a broad giant resonance peak more complex than the sharp resonance peaks of the transitions to the localized states of ${}^3P_1$ and ${}^3D_1$.

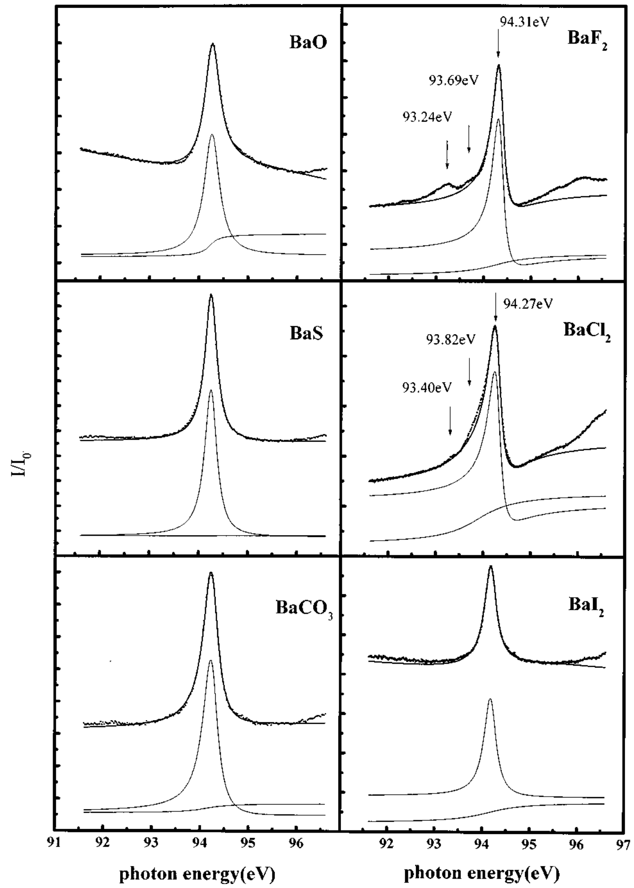

FIG. 2. The photoabsorption peaks of Ba $4d^{10}\,{}^1S_0$ to $4d^9 4f^1\,{}^3D_1$ and their curve fits for various barium compounds. Curves of Fano profile and arctangent as well as their combinations are shown for each compound. The energies of the satellites of BaF$_2$ and BaCl$_2$ are indicated.

The resonance spectra of $4d^{10}\,{}^1S_0$ to $4d^9 4f^1\,{}^3D_1$ of all samples taken by the fine-step scans are shown in Fig. 2. Two low-energy satellites of BaF$_2$ and BaCl$_2$ are clear seen as marked in the figure. Such satellites are not so apparent in the other samples. In comparison with the spectral lines of barium vapor[1,2] in the energy range of 92 to 97 eV, one notes that all the spectral lines of barium vapor are suppressed but the one corresponding to the transitions to the final states, $4d^9 4f^1\,{}^3D_1$. The suppressed spectral lines are mostly from the transitions of $4d^{10}$ to the $4d^9 6s^2 6p^1$ multiplet. The spread of the Ba $6p$ state of barium ions in solid compounds may be the reason of the suppression. The spread of Ba $6p$ states in solid compounds can be envisioned from its possible contribution to the density of states in the valence band of barium solid compounds as observed in x-ray emission spectra.[12]

Presumably, the satellites visible in the spectra of BaF$_2$ and BaCl$_2$ are the ''suppressed'' spectral lines aforementioned. The one at about 93.69 eV in BaF$_2$ as well as the one at about 93.82 eV in BaCl$_2$, next to the main resonance peak, is close to the energy of the spectral line in barium vapor at the energy of 93.78$\pm$0.08 eV.[2] This line was classified as the transition to the final state of $4d^9({}^2D_{5/2})6s^2 6p({}^2P_{3/2})$.[2,13] Its intensity was observed comparable to the spectral line of the transition to the final state of $4d^9 4f^1\,{}^3D_1$ in Ba vapor, but it is suppressed a great deal in BaF$_2$ and BaCl$_2$, and almost invisible in the other solid compounds. However, no spectral lines in Ba vapor can be found to correspond to the satellite

TABLE I. The peak energy of the photoabsorption line of Ba $4d$ for the transition of ${}^1S_0$ to ${}^3D_1$ of some barium compounds. The line width Γ and the asymmetry parameter q from the curve-fit analysis (see text) are also shown. N is the coordination number of the nearest ligand, R is the average bonding length, and η is the coordination charge.

	E (eV)[a]	Γ(eV)	q	N	R (Å)	$\eta = ZI$
BaO	94.22(2)	0.38	−70.0	6	2.76	1.60
$BaCO_3$	94.19(2)	0.37	−10.0	6	2.58	
BaS	94.21(2)	0.30	−33.0	6	3.19	1.02
BaF_2	94.31(2)	0.31	−3.5	8	2.68	1.82
$BaCl_2$	94.27(2)	0.38	−2.7	6	3.24	1.44
BaF_2	94.16(2)	0.32	−7.0	6	3.61	1.08

[a] The number in the parenthesis is a probable error of the last digit of the energy E.

whose energy is farther below that of the main resonance peak; about 93.24 in BaF_2, and about 93.40 in $BaCl_2$. Another interesting phenomenon is that the spacing between the satellite to satellite, and the satellite to the main resonance peak in BaF_2 is larger than that in $BaCl_2$. A calculation including the solid-state effect may be needed to fully understand them. Hereafter, we shall focus our attention on the main resonance peak of the transition of Ba $4d^{10}$ to $4d^9 4f^1\ {}^3D_1$ only.

The line shapes of the spectral lines as shown in Fig. 2 vary with the chemical compounds and appear to be a Fano profile.[14] In order to obtain a rather good fit, an arctangent background must be included. The instrumentation width, about 50 meV, is neglected in these fittings. The fitting curves are also shown in Fig. 2. The resonance energies E, the line widths Γ, and the asymmetry parameter q are listed in Table I for all the compounds we studied. The resonance energy E as well as Γ and q in $BaCl_2$ can be interfered by the nearby satellite. The line width seems to be overestimated. But the effect on the resonance energy E should be much smaller, since the peak height of the main resonance peak is relatively large and the separation from the nearest satellite is about 0.45 eV larger than the line width of about 0.3 eV. The probable error of the peak energy introduced by the measurement has been carefully examined through the repeated experimental runs. After the energy calibration, by refer to the Al L main absorption line of α-Al_2O_3 as 78.80 eV, the peak energy of the absorption spectrum as determined by its first derivative is found with the error of about 0.015 eV. The peak energy so obtained is in fact the same as that derived from the curve-fit analysis within the probable error of 0.02 eV.

In Table I, we also list the coordination numbers of the nearest ligands N, the average bond length R (calculated from the crystal structure data[15]) and the coordination charge η defined as ZI, where Z is the formal valence of Ba, and I is the single-bond ionicity, which is

$$I = 1 - \exp\left[-\tfrac{1}{4}(\chi_A - \chi_B)^2\right].$$

χ_A and χ_B are, respectively, the electronegativity of the metal and the ligand as scaled by Pauling.[16]

One notes that peak energies corresponding to the transition of Ba $4d^{10}\ {}^1S_0$ to $4d^9 4f^1\ {}^3D_1$ in barium halides are different from those of BaO, $BaCO_3$, and BaS. The peak energies of the halides vary with their coordination charges relatively well; when the coordination charge is large, the peak energy is large as shown in Fig. 3. Here we plot the peak energy vs the Ba-coordination charge. The data are given in Table I. The trend of the variation of the halides is understandable, since a larger coordination charge means a larger ionicity and thus the chemical shift will be towards the higher energy. It is then somewhat peculiar for BaO, $BaCO_3$, and BaS in the same term, for their peak energies being close to each other, yet their coordination charges are quite different. It however becomes clear when Fig. 3 is examined closely, where the data of $BaCO_3$ is also included by assuming that it has the same coordination charge as BaO. One observes that the position of the oxides, BaO and $BaCO_3$, are away from the ''main trend'' as indicated by the eye-guided dot line. This may indicate that the coordination charge as presented in Table I is no longer suitable to describe the coordination charges of the oxides. One of possible explanations for it may rest on the fact that the Ba electrons contribution to the valence band of the oxides is mainly the electrons of Ba $5d$ in character,[5] while the other compounds are Ba $6s$ in character. Then the localization of Ba $5d$ electrons in the oxides, due to its charge screening effect, can decrease the coordination charge of Ba ions in the oxides such that the value in Table I is overestimated for BaO.

IV. SUMMARY

High-resolution photoabsorption spectra of Ba $4d \rightarrow 4f$ in the barium compounds of BaO, BaS, BaF_2, $BaCl_2$, BaI_2, and

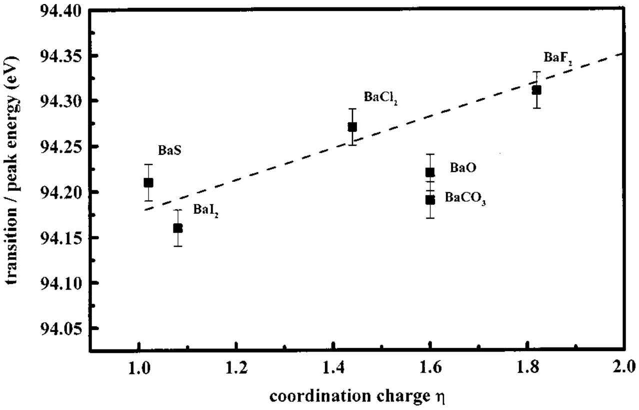

FIG. 3. The transition energy of Ba $4d^{10}\ {}^1S_0$ to $4d^9 4f^1\ {}^3D_1$ versus the Ba-coordination charge (see text) for BaO, $BaCO_3$, BaS, BaF_2, $BaCl_2$ and BaI_2. The dot line is the eye-guided line for the ''main trend'' compounds.

$BaCO_3$ have been measured by Synchrotron radiation at SRRC in Taiwan, R.O.C. The two distinguished photoabsorption lines observed in this work are identified to be atomlike spectra of Ba ions arising respectively from the transitions of $4d^{10}\ {}^1S_0$ to $4d^94f^1\ {}^3P_1$ and $4d^94f^1\ {}^3D_1$. Below the resonance peak of ${}^1S_0$ to ${}^3D_1$, some satellites are found in the solids of BaF_2, and $BaCl_2$. No such satellites can be identified in the other compounds. The peak energies have been determined by a curve-fit analysis. The transition energies of ${}^1S_0$ to ${}^3D_1$ of barium halides are found to follow the coordination charge of the barium ions as calculated by a simple formula relatively well, larger for larger coordination charge. But it is not so for BaO and BaS, for their coordination charges are different, yet their photoabsorption energies are similar. The characters of the electrons of Ba contribution to the valence band of the halides and the oxides are suggested to be different. The latter is mainly Ba $5d$ in character, while the former is mainly Ba $6s$ in character.

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