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Comprehensive Survey of Oxygen X-Ray Emission Band Shifts

B. Krause and E. W. White

TECHNICAL REPORT NO. 2

Office of Naval Research, Metallurgy Program

Contract No. N00014-67-A-0385-002, NR 032-502

8 AUGUST 1963

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COMPREHENSIVE SURVEY OF OXYGEN X-RAY EMISSION BAND SHIFTS

by

B. Krause and E. W. White

ABSTRACT

Shifts in the oxygen K-emission band from some fifty simple oxide compounds have been studied as part of a program to evaluate soft x-ray spectroscopy as a tool for characterizing thin layers on metals. The main peak tends to shift to shorter wavelength as the valence of the coordinating cation increases. For oxides of transition metal element one can determine the cation valence from the O-K α position. For the oxide of the non-transition metals the oxygen peaks tend to be relatively narrow and exhibit little or no resolved fine structure. For oxides containing highly charged cations the O-K β ' band becomes a well-resolved feature on the long wavelength side of the main peak.

INTRODUCTION

Oxygen is undoubtedly the most ubiquitous element. In spite of this fact, it is the least studied by direct techniques. Methods for direct analysis are generally lacking and even the analytical chemist generally arrives at the oxygen content indirectly by difference. Typically the role of oxygen in a given metal-oxygen system is determined either by x-ray structure analysis or by studies of the metal cation. Unfortunately, most structural analysis tools fail completely for amorphous materials.

We have felt for some time that x-ray emission spectroscopy promised to become one of the most powerful tools for the study of

oxides. Recently we have obtained an analyzing crystal which gives exceptionally good results for oxygen both in terms of peak intensity and spectral resolution. The $OK\alpha$ is the principal oxygen x-ray line and x-ray emission band. It results from electron transitions from the valence band of oxygen (2p band) to the K-shell. It is generally understood that the peak intensities of emission bands are not directly useful for quantitative analysis but on the other hand the emission bands are particularly sensitive to the chemical state of the emitting atom. Thus, although it may prove difficult to quantitatively analyze for oxygen, one should hope to use the $OK\alpha$ to establish something about how the oxygen is chemically combined. The line shifts are caused largely by changes in the effective charges due to the removal or the addition of the valence electrons. Furthermore, it has been found that the molecular character of the compound has an influence on the line position. Theories reported in the literature are not yet capable of quantitatively predicting spectra, and the experimental data in the case of oxide spectra are rather scarce.

Chun and Hendel¹ found by the use of a high resolution spectrometer that the oxygen K-emission band is a complex of 6 lines. (Probably all the curves in Chun and Hendel's paper are plotted on a nonlinear intensity scale which has the effect of exaggerating the low intensity features.) The unresolved $K\alpha$ doublet is the strongest line of the spectrum. On the high energy side of the main peak they observed the α_3 , α_4 , α_5 , and α_6 satellites. On the low energy side occurs the β' satellite which probably can be explained as valence electron configuration states as predicted by Parratt². All lines vary both in position and intensity from oxide to oxide. However, the only correlation which

they found between the experimental data and crystal chemical parameters was with the electronegativity of the elements forming the oxide.

With this sort of background in mind we asked the following questions:

- 1) Is it possible on a given metal substrate to determine which oxide phase was formed simply by studying the oxygen K-emission band?
- 2) Can one say anything about the chemical state of oxygen dissolved in a metal?

EXPERIMENTAL

All the oxygen K-emission bands were recorded using an ARL model EMX electron microprobe. The microprobe was operated at 20 keV and 0.1 μA with a 100 μm diameter beam size. A specially mounted clinchlore crystal ($2d = 28.36\text{\AA}$) was bent to an eight inch radius for use on the four inch ADP spectrometer. This crystal gave exceptionally good results for oxygen both in terms of peak intensity and spectral resolution. The peaks were scanned at approximately 0.03 $\text{\AA}/\text{min}$. The count rate varied from about 20 to over 500 cps. A typical count rate was about 200 cps. Each peak was recorded in triplicate and all wavelength measurements were made with respect to the oxygen peak from quartz ($\alpha\text{-SiO}_2$), the quartz peak was arbitrarily assigned the value of 23.60 \AA . The data were screened for higher order interference peaks. Tracings of many of the bands are reproduced in the figures to illustrate shape changes. The individual peaks are unresolved, however, a $K\beta'$ satellite can be recognized on the long wavelength side and $K\alpha_3\alpha_4$ satellites on the short wavelength side of many of the tracings. The

$\alpha_{5,6}$ satellites were not observed; they are probably hidden in the background and therefore the tracings were not extended to correspondingly short wavelength.

RESULTS

Figure 1 shows the oxygen K-emission bands for a series of titanium oxides. With increasing reduction there is a shift of the main line towards longer wavelength. In addition, the low intensity $OK\beta'$ peak on the long wavelength side of the spectrum weakens and the OK_{α_3, α_4} on the low angle side appears to come in. There is a small but significant difference between the bands from anatase and rutile.

A similar line shift with a decreasing percentage of oxygen can be observed in a vanadium-oxygen series (Fig. 2), in a manganese oxide series (Fig. 3), and in an iron-oxide series (not shown). On the other hand no such shifts occur in a lead oxide series (Fig. 4).

Figure 5 summarizes the shift measurements for three sets of transition metal oxides and a set of lead oxides. In the figure all peak shifts were measured with respect to the oxygen peak from α -quartz. Peak positions were determined at $2/3$ peak height.

It appears that the d-electron configuration plays an important part in the peak geometry; vanadium, manganese and iron are transition metal oxides and consequently the $OK\alpha$ peaks of their oxides show similar trends. The bonding in lead, on the other hand, does not involve d-electrons, and the oxide K-spectrum behaves differently.

The difference type of bonding of transition metals on the one hand and metals with filled d-shells on the other manifests itself clearly in the spectra of the MeO series ($Me = Metal$) as shown in

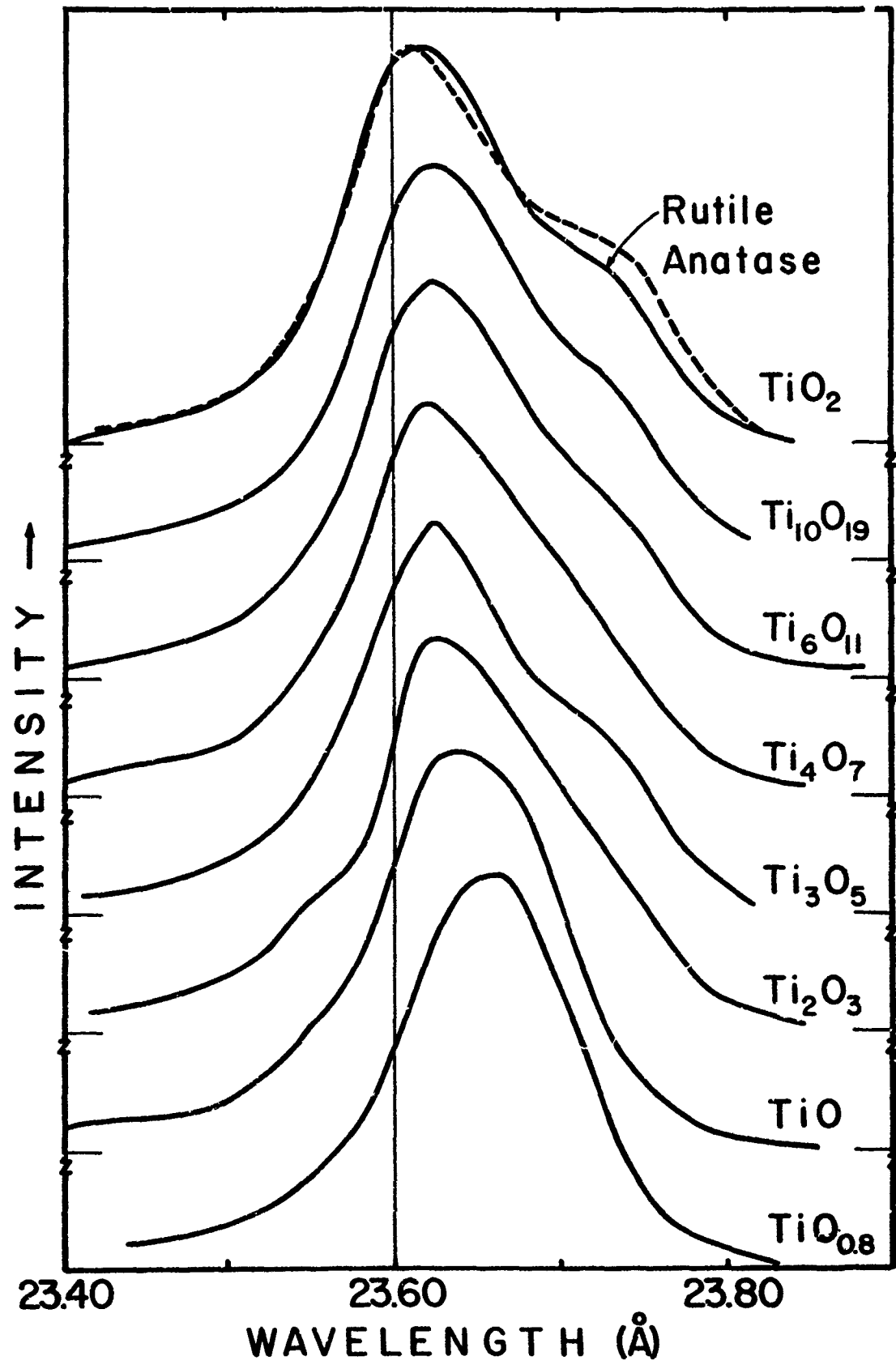


Fig 1

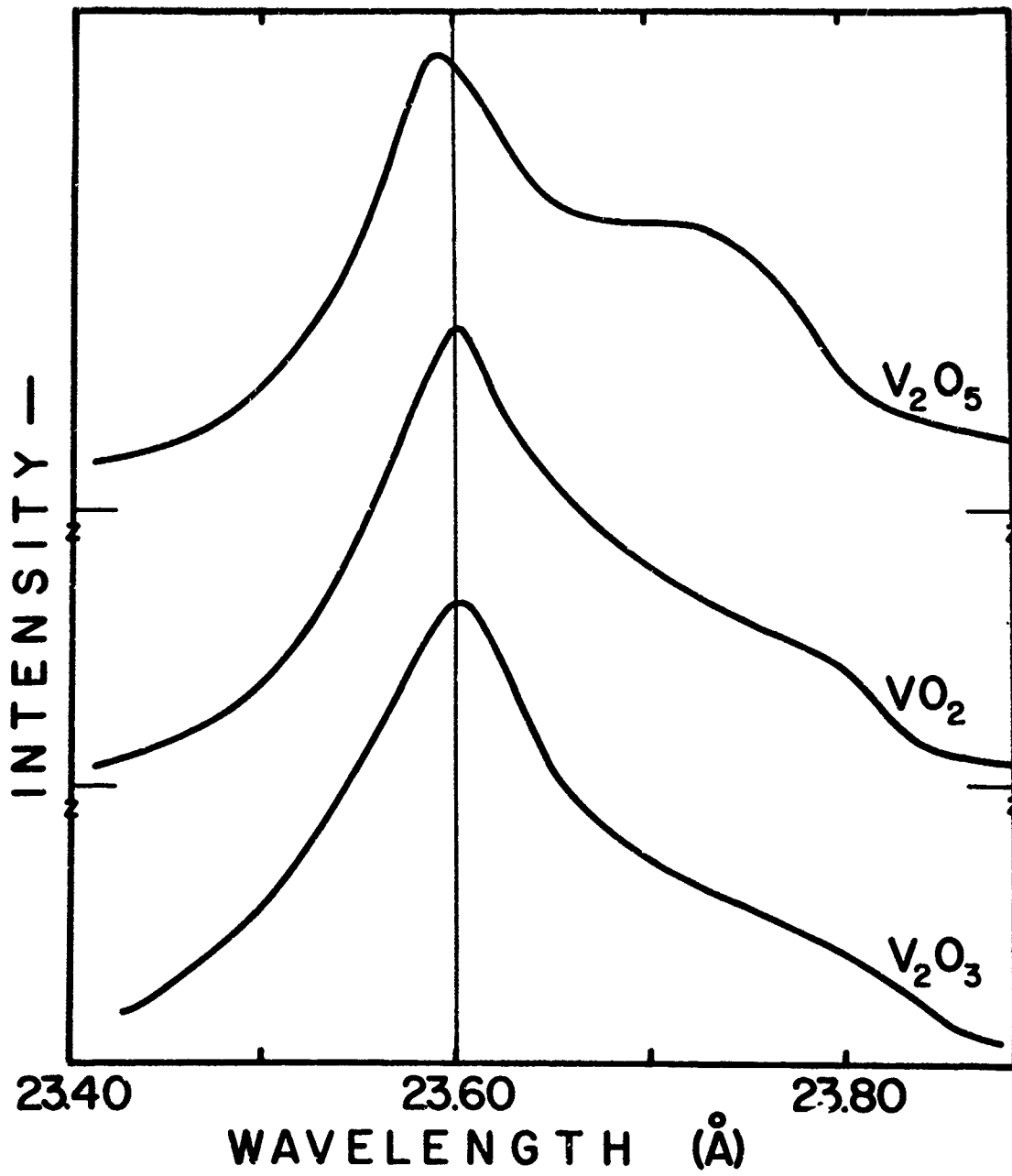


Fig. 2

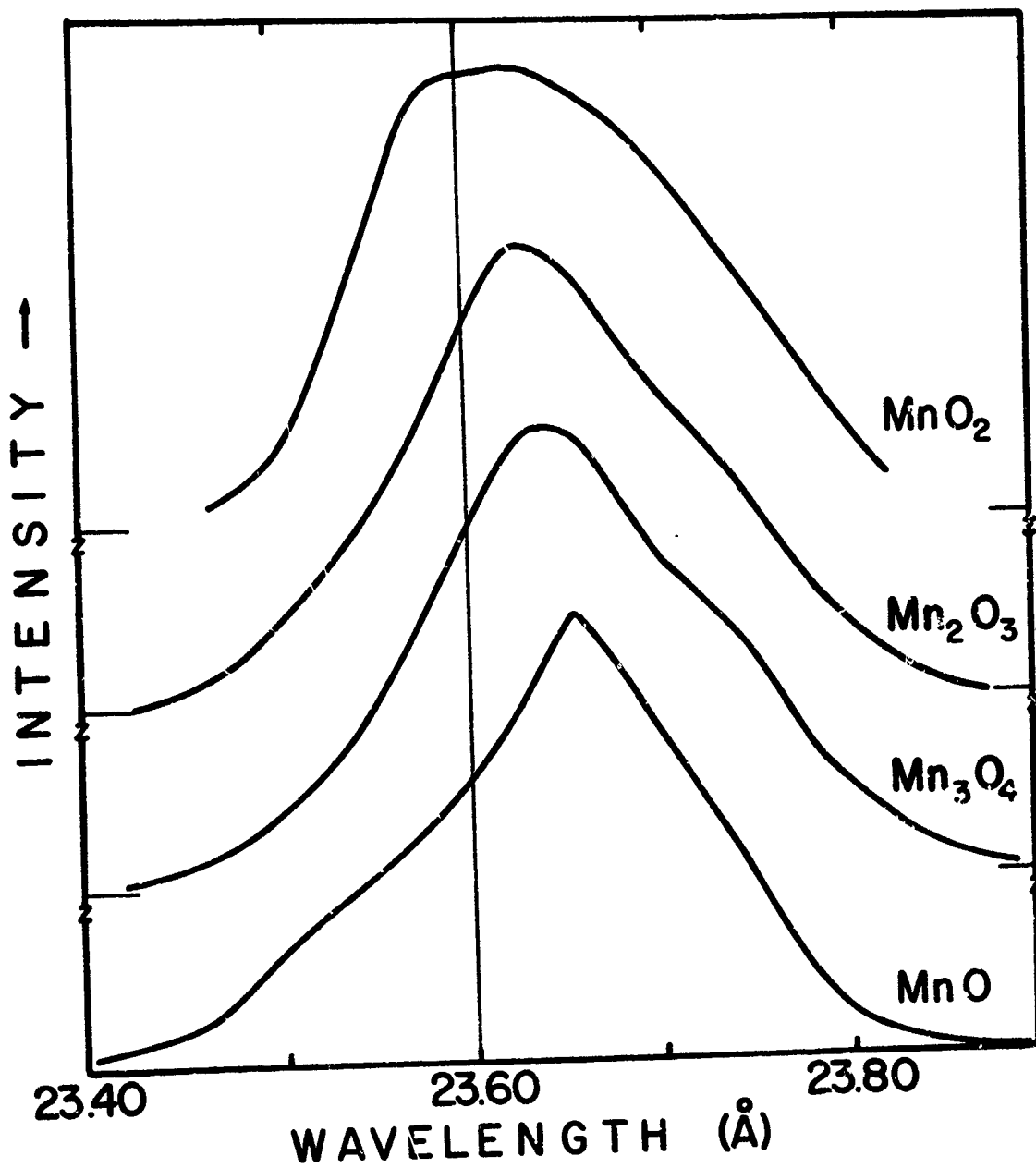


Fig. 3

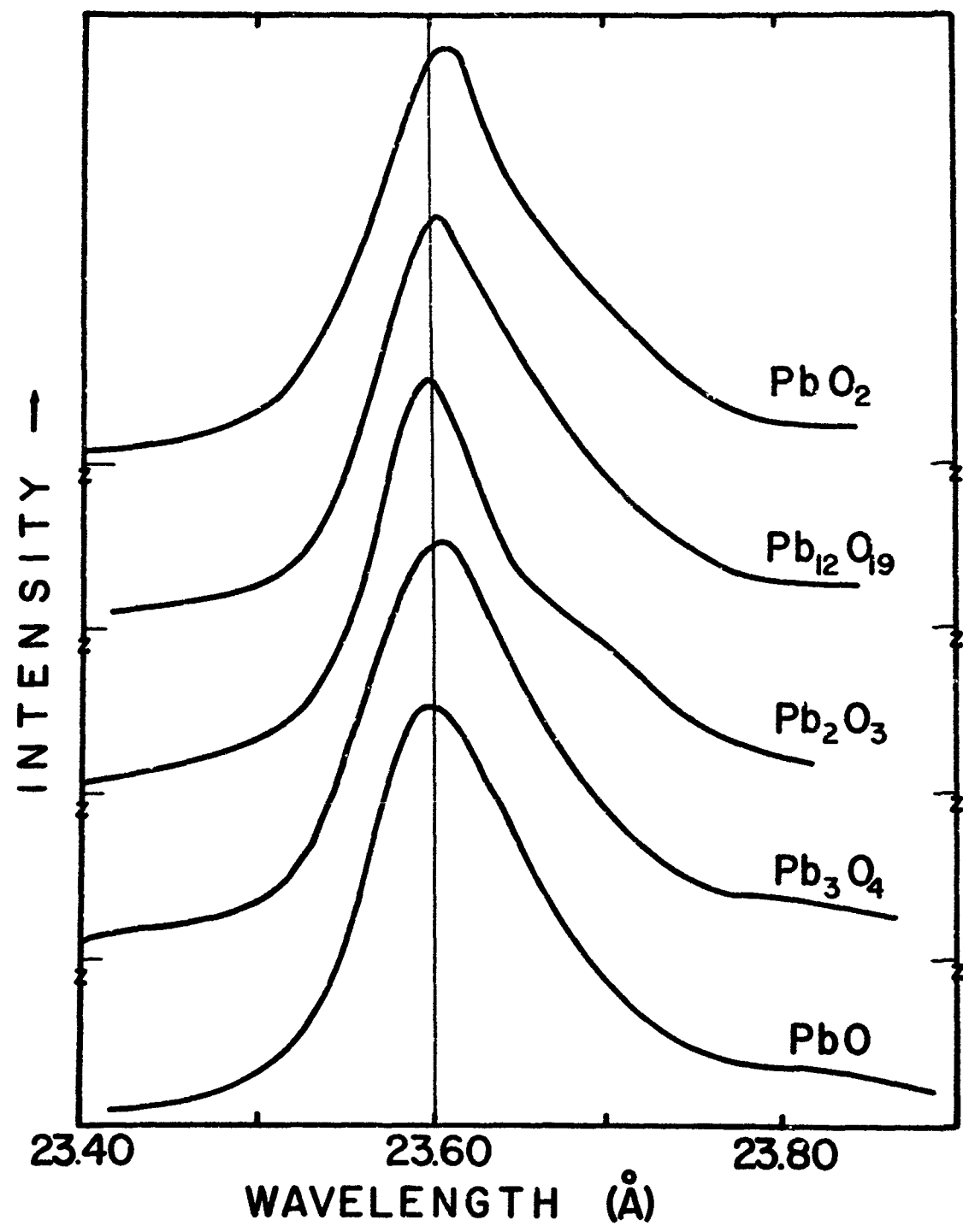


Fig 4

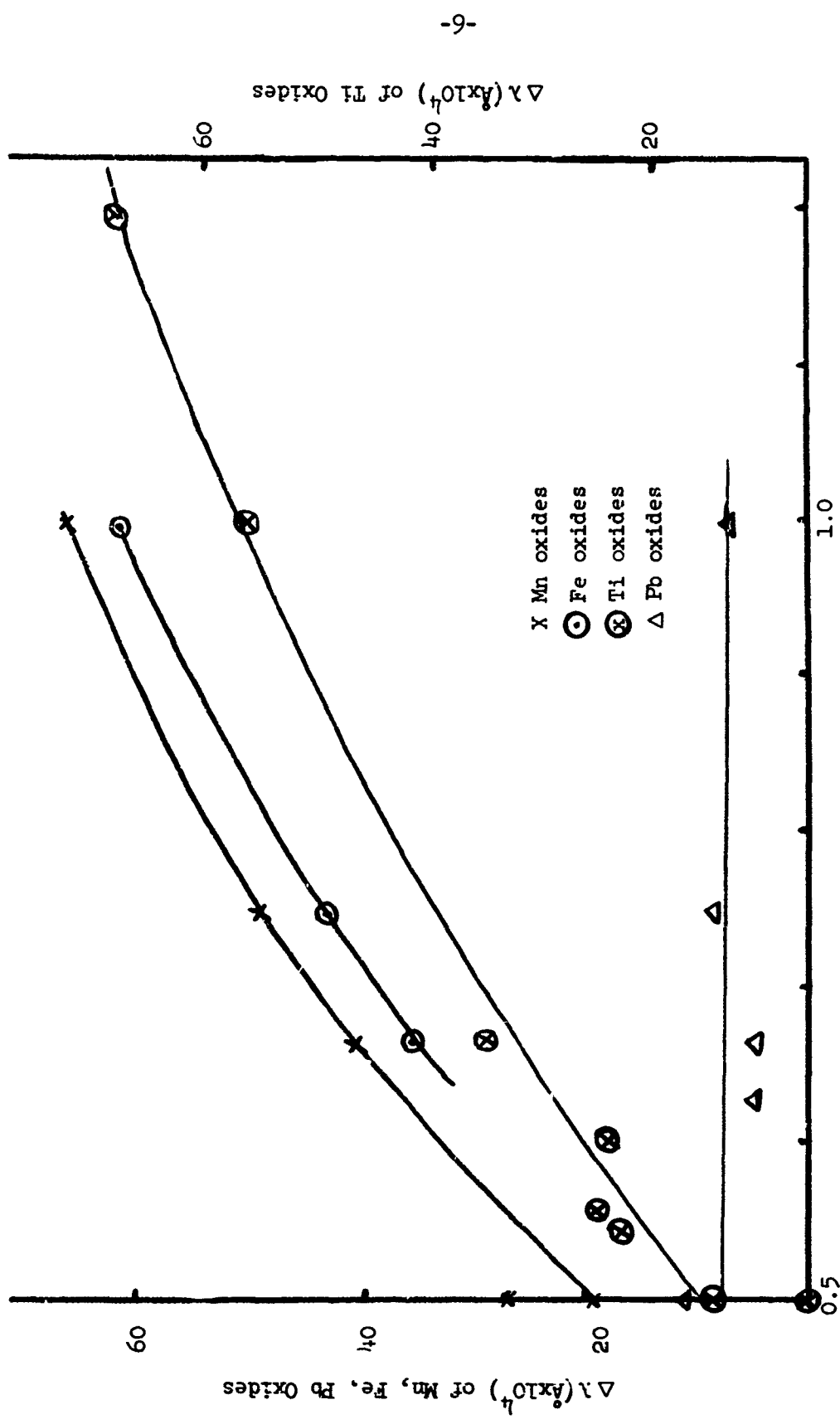


Figure 5 Molar Ratio $\frac{\text{metal}}{\text{oxygen}}$

Fig. 6. The series is ordered according to increasing atomic number of the metal. The transition metal series TiO, MnO, FeO, CoO, NiO and CuO show similarities. With increasing number of d-electrons, the main peak shifts towards longer wavelengths and a low wavelength peak appears to come in. The differences between the line profile of CuO with an unfilled d-shell and ZnO are striking. The character of the bonding in CdO, HgO and PbO is strongly covalent. It is, therefore, not astonishing that the curves differ markedly from those of the transition metals when the bonding is more strongly ionic.

Figure 7 shows a MeO_2 series of compounds which crystallize in a rutile structure. The difference between oxides with filled d-shells and those with unfilled d-shells is again very obvious. In the one case the peaks are comparatively narrow, in the other case they are broad. The differences between TiO_2 (anatase) and TiO_2 (rutile) or GeO_2 (quartz) and GeO_2 (rutile), respectively, are much smaller than those between different compounds within the rutile series.

The line shapes from two MeO_3 compounds (Fig. 8) are very similar. The same holds true for MeO_2 curves for compounds with the corundum structure (Fig. 9). In fact, there is a close resemblance between CeO_2 , ThO_2 and the rutile type compounds with filled d-shells.

It was noted that in the oxides of highly charged cations (Figs. 8 and 10) that the intensity of the curves decays only very slowly towards the long wavelength side. In other words, the $OK\beta'$ band becomes stronger with respect to the $OK_{\alpha_1\alpha_2}$. In the vanadium series (Fig. 3) the $OK\beta'$ band is clearly resolved for V_2O_5 . It becomes weaker with decreasing valency of the metal. In general, the line profiles become more symmetrical as the metal valency decreases. The Me_2O_5 compounds (Fig. 10)

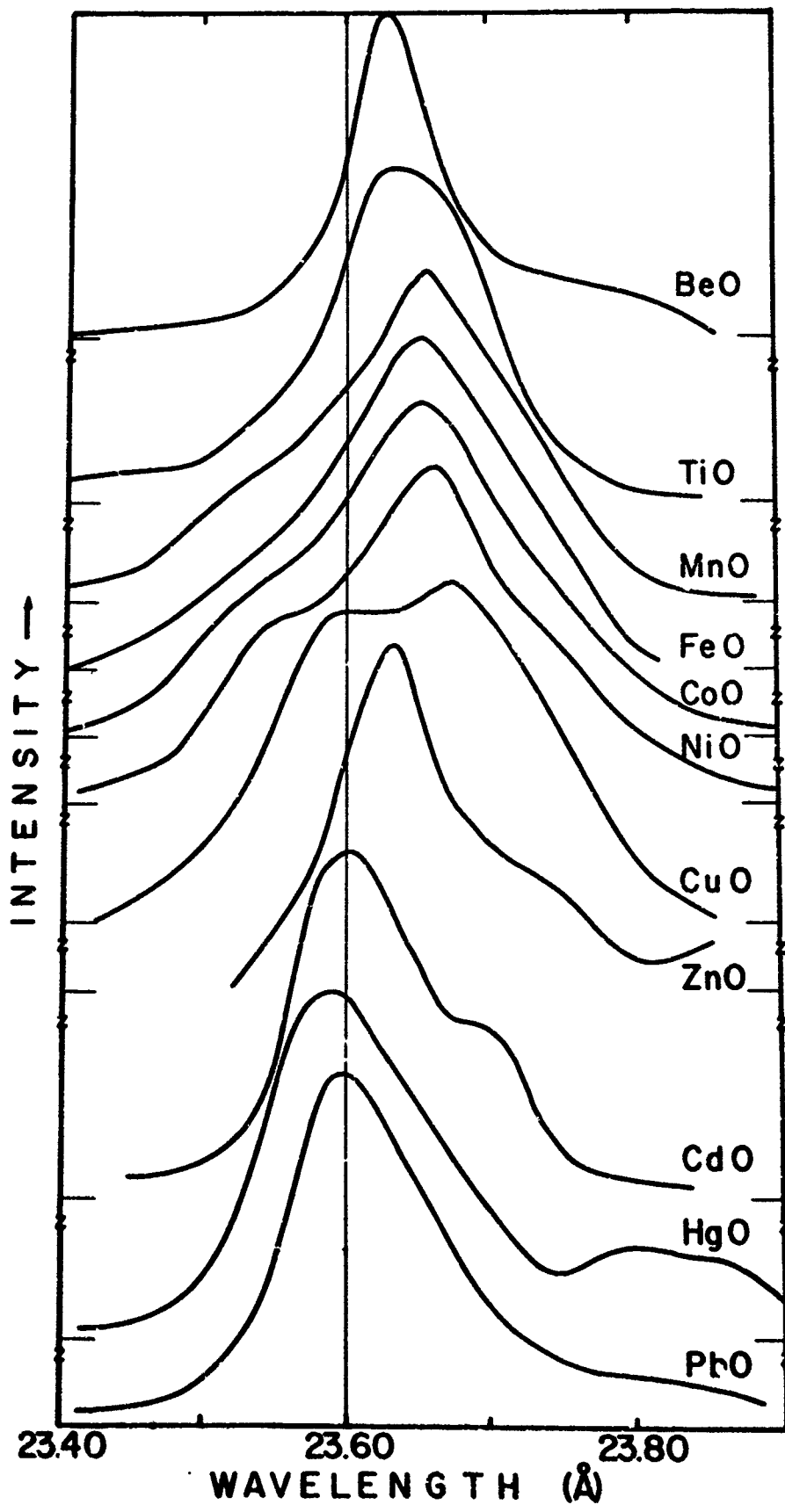


Fig. 6

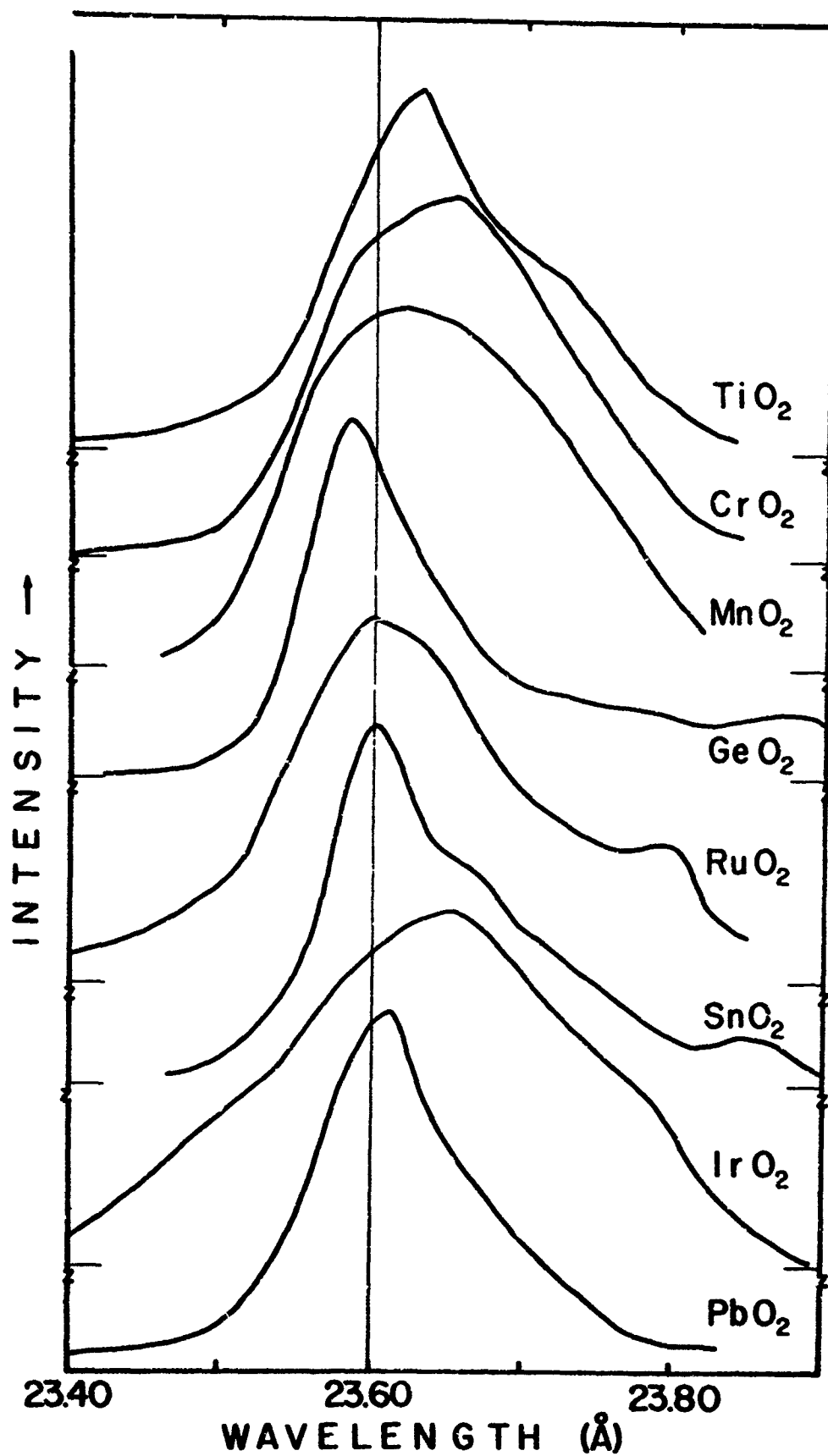


Fig. 7

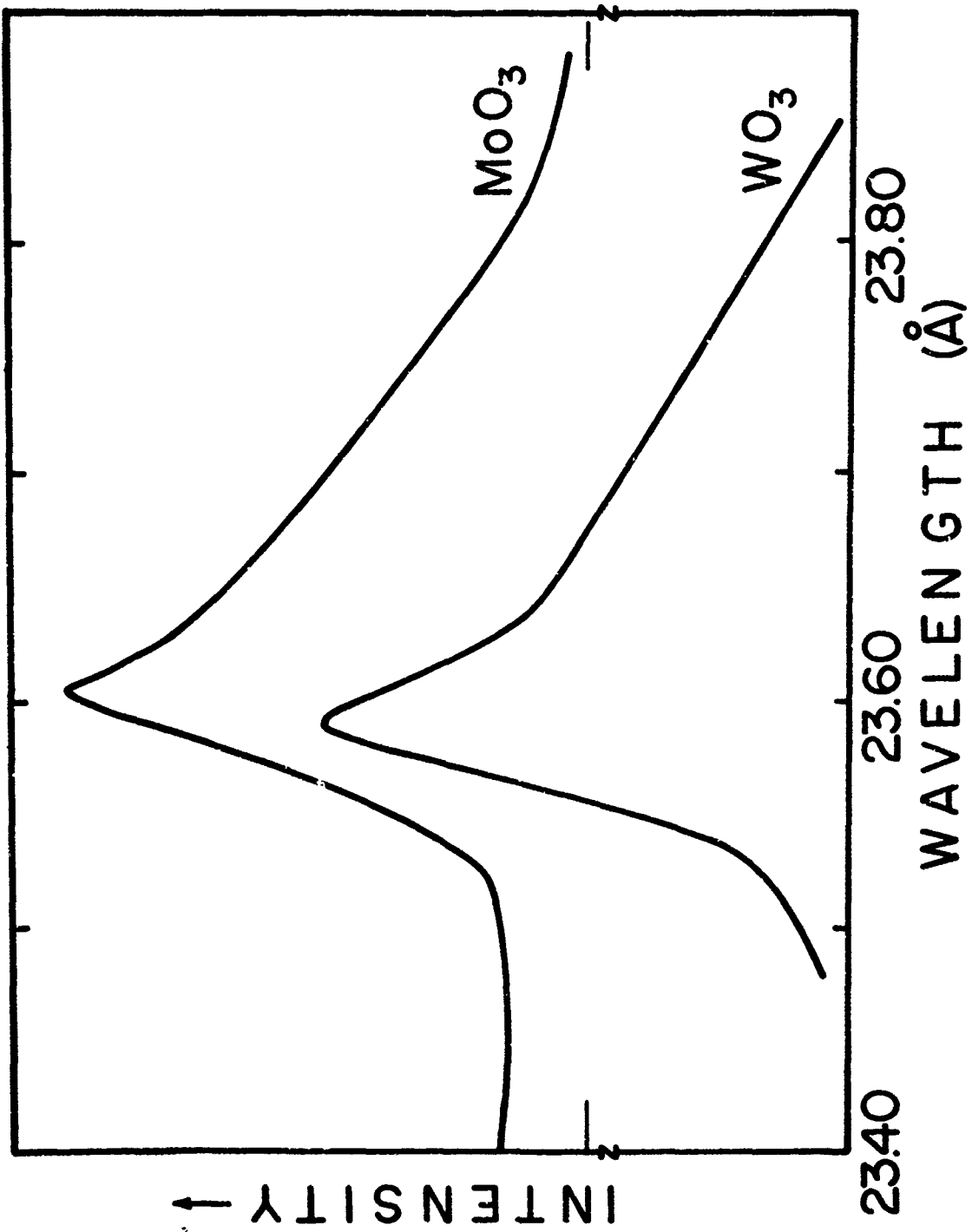


Fig. 8

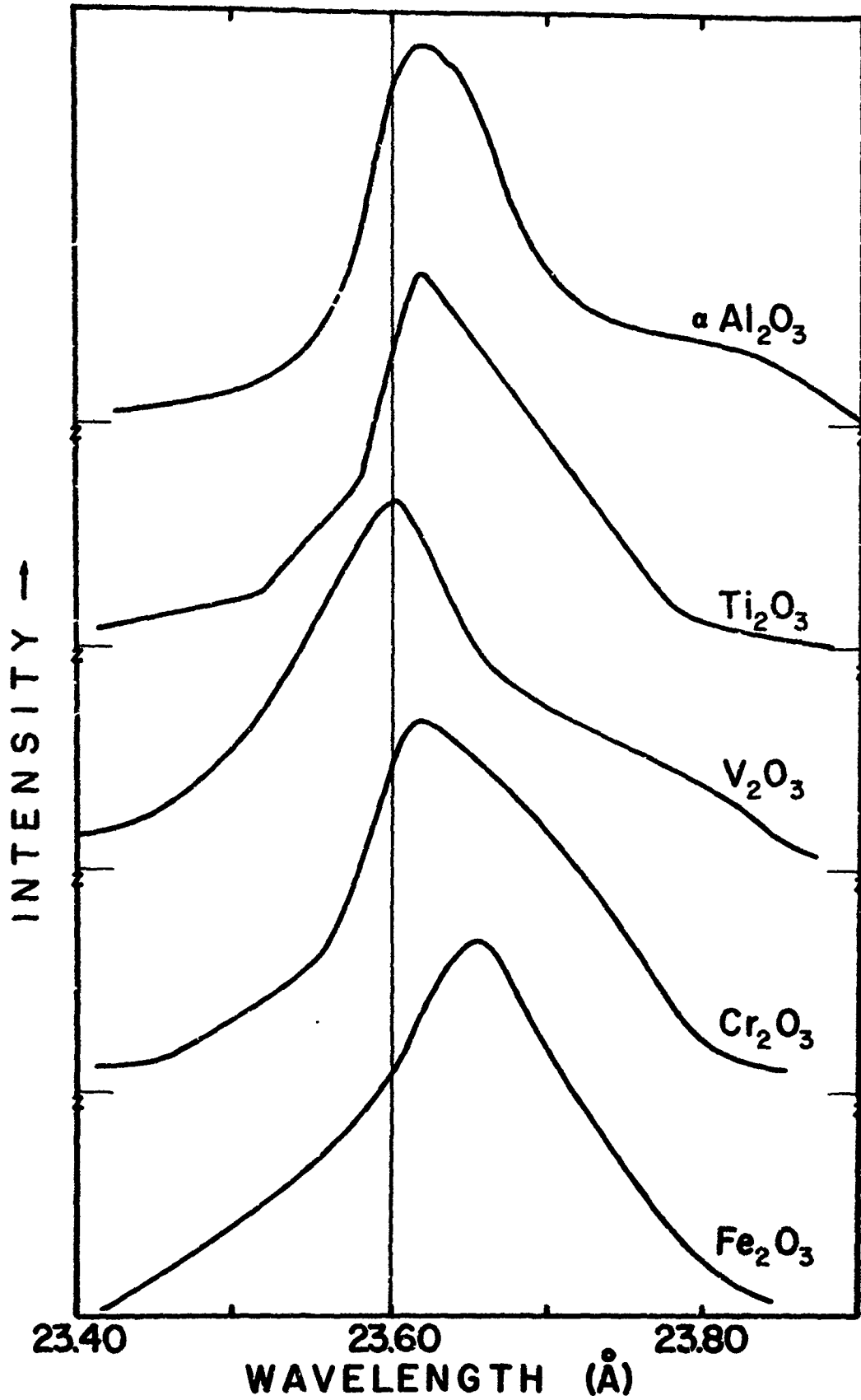


Fig. 9

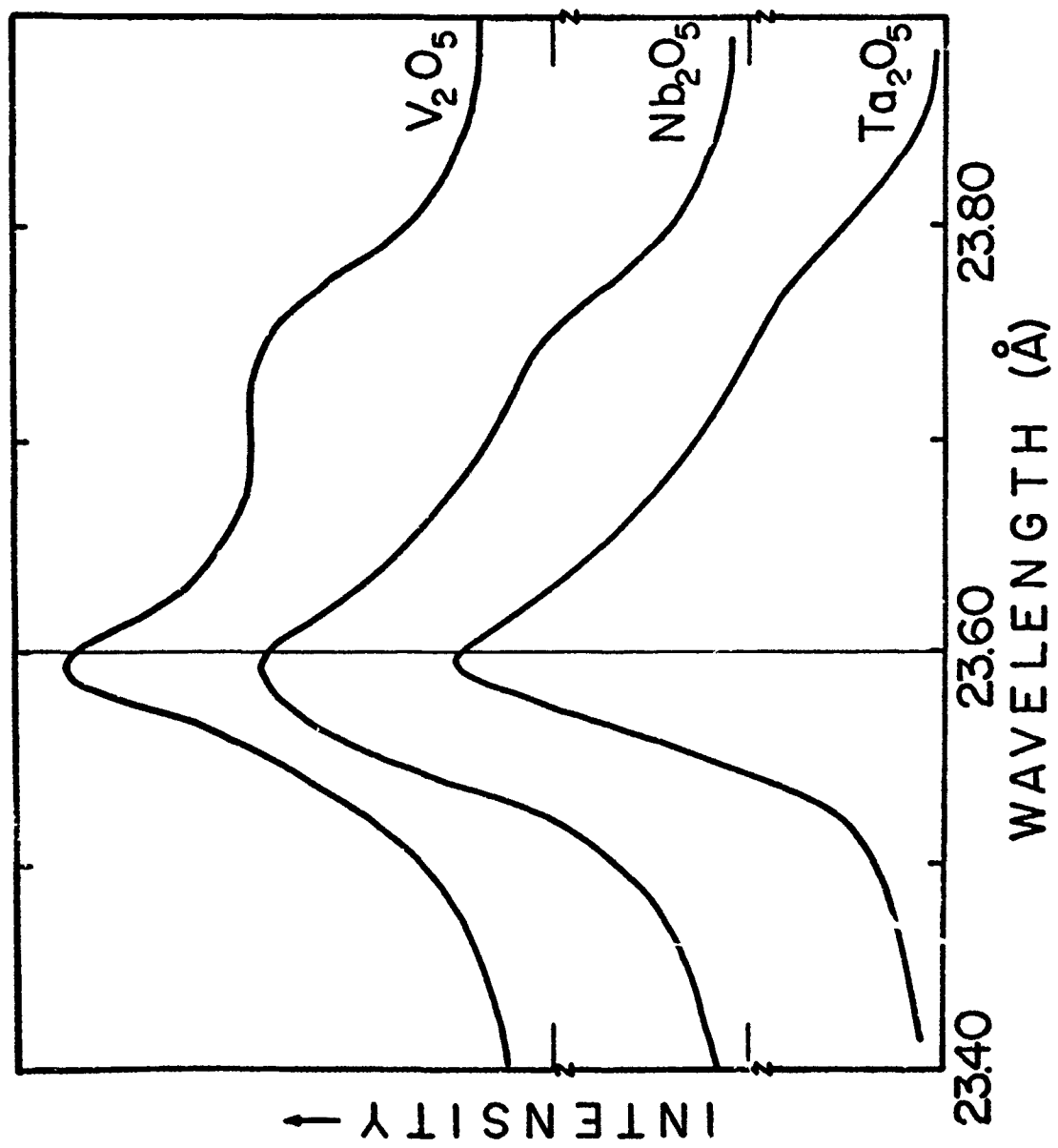


Fig. 10

show a significant $OK\beta'$ tail whereas the series Me_3O_4 show almost symmetrical peaks (Fig. 11). In the transition metal series of the MeO compounds, on the other hand (Fig. 6), there is sometimes a pronounced low wavelength tail due to partially resolved $OK_{\alpha_3\alpha_4}$ satellite lines.

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2. L. G. Parratt, "Electronic Band Structure of Solids by X-ray Spectroscopy," *Rev. Mod. Phys.* 31, 616-645 (1959).

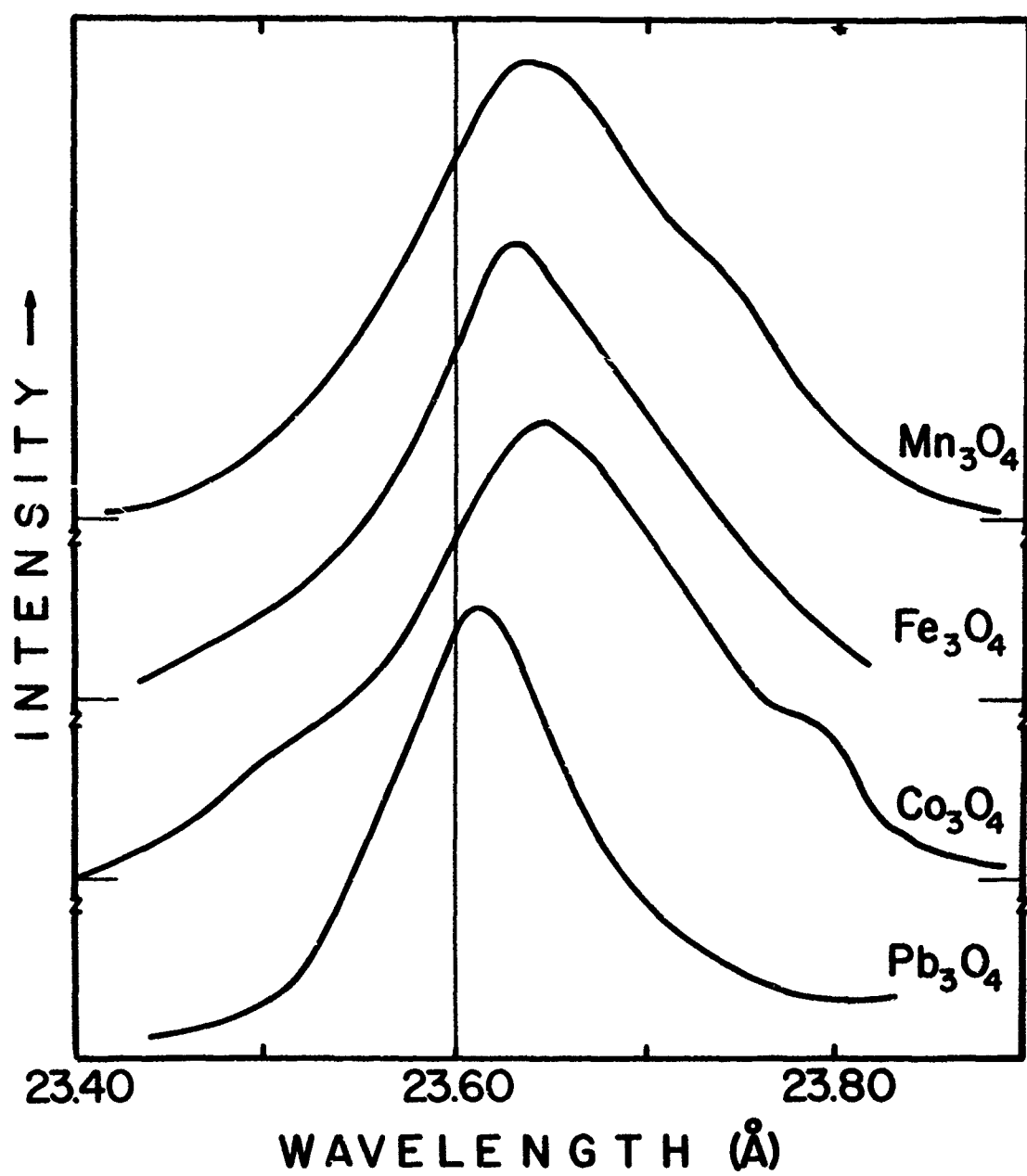


Fig. 11

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