Metallic and insulating $3d$ transition-element monoxides and their stability

Börje Johansson

Department of Physics, Försvarets Forskningsanstalt, Stockholm, Sweden

The binding properties of the $3d$ monoxides are studied in detail, and it is shown that the metallic character of TiO and VO is directly reflected in their heat of formation. The same holds true for NbO. From a stability analysis of the $3d$ monoxides versus decomposition, it is found that TiO, VO, and FeO are close to an instability. Further, it can be concluded that both ScO and CrO must be very near existence. The general occurrence of transition-metal monoxides is shown to be directly correlated with ionic properties of the transition elements. An investigation of the absorption edge in the $3d$ monoxides is also undertaken. The importance of the crystal-field splitting is noticed, and it is shown that the heat of formation of the monoxides can be used to derive the crystal-field parameter Δ. The change from a delocalized to a localized behavior of the d electrons in the $3d$ monoxides is compared with a similar change of the f electrons in the actinides. Some similarities between these two series of materials are pointed out.

I. INTRODUCTION

The monoxides of the $3d$ elements provide a series of compounds which is exceedingly well suited for a study of a localized versus a delocalized $3d$ behavior. All of them, except CuO, are isostructural, attaining the simple rock-salt structure, a circumstance which considerably simplifies the theoretical analysis. In the earlier $3d$ monoxides one finds a metallic behavior, which is in sharp contrast to the insulating state found in MnO and the heavier monoxides. Therefore, as a function of atomic number, there is a sharp change in the character of the monoxides. This may be directly correlated with the rather rapid $3d$ shell contraction which takes place when one proceeds to the heavier elements. Thereby, due to the decreased mutual wave-function overlap, the gain of kinetic energy in the delocalization is considerably reduced for the heavier elements. Equally important, the delocalization process must always take place at the sacrifice of correlation energy (the atomic $3d$ correlation, manifested by the Hund's rules, must be broken). Apparently, for the monoxides the gain in kinetic energy and loss of correlation energy become critical somewhere between vanadium and manganese.

The insulating behavior of the heavier $3d$ monoxides cannot be understood within the conventional Bloch-Wilson band theory. This has been thoroughly reviewed by Adler.[1] Instead, as already indicated, correlation dominates and the materials must be considered as Mott-Hubbard-like insulators.[2-5] Naturally, CaO, with a d^0 configuration, is an insulator already within the normal Bloch-Wilson scheme.

In the theoretical treatments of these compounds normally only the electric and magnetic properties are subjects of discussion. Further, it is mainly

from the conductivity point of view that the change from delocalized to localized behavior in the series has been inferred. Here, however, one of our purposes is to demonstrate that in fact there exist other experimental data, which strongly corroborate the idea about metallic behavior in the earlier $3d$ monoxides. Further, these data give considerable additional insight to the nature of the change of behavior through the series.

Another aspect, which also can provide a deeper understanding of the transition-metal oxides in general, is their stability or instability versus other oxidation numbers. This constitutes a huge and complicated problem and in this paper we will certainly only cover a small part of it. Of particular interest for an insulating monoxide is the $d^n \to d^{n-1}s$ excitation (corresponding to the absorption edge), and we will later indicate that this energy is directly related to the stability of the compound versus decay into a higher oxide system. Further, from the behavior of the $d^n \to d^{n-1}s$ excitation energy we may conclude that neither in TiO nor in VO will there be any occupation of the s band. Therefore, the delocalization of the d electrons in these two materials does not originate from s-electron screening in contrast to the suggestion made by Heine and Mattheiss.[6]

An interesting observation, which can be derived from a study of stability, is that hypothetical *insulating* TiO and VO could never exist. Instead they would rapidly decompose into higher oxides. Therefore, it is only the metallic character which rescues these two oxides from decomposition.

In the actinide series, the $5f$ electrons are itinerant for the earlier elements but form localized states in the heavier elements ($\geq$ americium). Therefore, the actinides become rare-earth-like only in the latter part of the series. This behavior certainly has very much in common with the $3d$
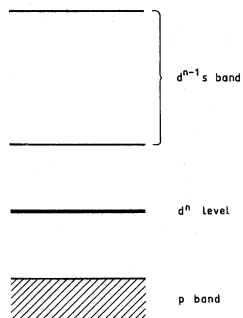
FIG. 1. Schematic representation of the energy level scheme for the insulating $3d$ monoxides.

monoxides and a comparison between the two series should be enlightening.

In Sec. II we consider the energy-level scheme of the $3d$ monoxides. Especially the $d^n \rightarrow d^{n-1}s$ excitation is treated in some detail. Section III contains an explicit demonstration of the metallic binding present in TiO and VO. Also the $4d$ monoxide NbO is shown to be metallic. This section also contains a study of the stability of the monoxides towards higher oxidation numbers. In Sec. IV we compare the $3d$ monoxides with the actinide series of elements. Finally, a discussion is given in Sec. V.

II. ENERGY-LEVEL SCHEME FOR THE 3d MONOXIDES

Morin[7-9] undertook a fundamental study of the physical properties of the transition-metal oxides, considered as a group of materials. More recently, Mattheiss[10,11] has made an important contribution to the understanding of the $3d$ monoxides, by performing augmented-plane-wave (APW) calculations for the whole series of the $3d$ monoxides. This approach certainly has its limitations, since the conventional band picture is not directly applicable to the insulating oxides. However, the aim of the calculation was to provide a starting point, from which a more basic discussion of their underlying electronic structure and its relation to important physical quantities could be pursued. As an appropriate extension of Mattheiss's work, we suggest spin-polarized band calculations for the heavier monoxides.

In Fig. 1 we give a schematic representation of the level scheme for the insulating monoxides. The separation between the occupied p band and the unoccupied s band is appreciable (of the order of 5-10 eV). Somewhere between these two bands we find the atomiclike d^n level. It should be remarked that Mattheiss calculates a d-band width of about 4 eV. From photoemission experiments, however, one has found evidences for a much smaller width[12]—indicating an upper limit of about 1 eV. These bandwidths should be interpreted as

the width of the lower Hubbard "pseudoband"[13] and not as a normal bandwidth. This aspect has also been indicated in the notation of Fig. 1, where the position of the d^n level relative to the s band, actually involves a transition to a $d^{n-1}s$ state. Thus, the *local structure* of the d^{n-1} configuration is of importance and it is therefore not possible to use a band calculation for a comparison with the experimental absorption edge.

In Mattheiss's calculation, it was found that the energy separation between the d state and the s band decreases smoothly when going from the heavier to the lighter oxides. For *hypothetical insulating* VO (i.e., with a lattice constant appreciably larger, ~7%, than the experimental one) it was actually found that this energy separation becomes zero. This finding led Heine and Mattheiss[6] to suggest that the metallization of the d state in VO actually is driven by a partial occupation of the s state. Thereby, they argued, the additional screening from s electrons supports the delocalization of the d level. However, having in mind the mixed-valence compounds found for some rare-earth systems, it could also be quite tempting to apply the interconfiguration fluctuation (ICF) model[14,15] to this situation. Namely, that the d^3 and d^2 configurations of vanadium retain their atomiclike character, but undergo rapid spontaneous fluctuations from one to the other. At the same time a corresponding appreciable nonzero average occupation number of the s band should be maintained. However, there are several objections against such an interpretation, the main being, as we will demonstrate below, that the d level does not in fact overlap the s band, neither for TiO nor for VO.

From the calculated smooth variation of the d-s separation through the insulating series of monoxides, Mattheiss noted the difficulty to account for that experimentally MnO and NiO have been found to have absorption edges located at the same energy. However, for localized states, the atomic correlations should persist and the true separation between the s and d states must retain very much of its behavior for the free atoms. To get an idea of the variation of this separation, we have in Fig. 2 plotted the $d^n \rightarrow d^{n-1}s$ excitation for the divalent ions of the $3d$ elements. As can be seen, the variation from element to element is far from a smooth one. Were it not for the appreciable crystal-field effect on the d levels in the oxide compounds, a very similar variation as in Fig. 2 should be found for the absorption edge in these materials. Since the lattice constant does not vary too much for the insulating $3d$ monoxides we can with a rather good accuracy assume a constant reduction of the free ion $d^n \rightarrow d^{n-1}s$ excitation energy throughout the whole series of insulating com-
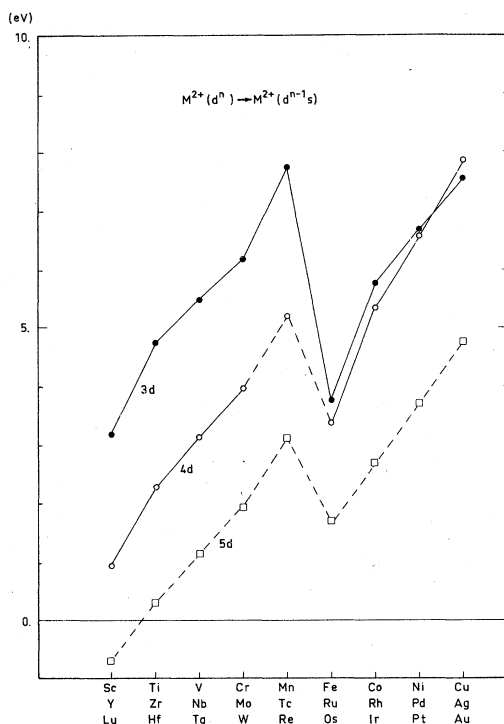
FIG. 2. $d^n \rightarrow d^{n-1}s$ excitation energy for free divalent ions of the transition elements. The experimental values for the $3d$ and $4d$ series are from Ref. 16. The value for lutetium is from Ref. 17. The other excitation energies (connected with dashed lines) are derived by the present author from considerations of excitation energies in the free atoms and singly ionized atoms.

pounds. Superimposed on this effect there is the crystal-field splitting of the d level. Assuming a constant crystal-field parameter Δ of about 1 eV (see below) for all the monoxides, this implies that the $d^n \rightarrow d^{n-1}s$ excitation will be further reduced by this energy Δ in the case of CrO and MnO (as well as in hypothetical NaCl structure CuO and ZnO) *in comparison* with the other $3d$ monoxides. The experimental absorption edge in NiO is found at 3.7 eV.[18] For the free divalent nickel ion the $d^n \rightarrow d^{n-1}s$ excitation energy is 6.7 eV.[16] Thus we find that the general reduction of this free-ion excitation energy is about 3 eV for the $3d$ monoxides. From this and the constant crystal-field assumption throughout the series we derive the following absorption edge energies for insulating monoxides (compare Fig. 2): ScO 0.2 eV; TiO 1.7 eV; VO 2.5 eV; CrO 2.1 eV; MnO 3.7 eV; FeO 0.7 eV; CoO 2.8 eV; NiO 3.7 eV; CuO 3.5 eV; and ZnO 5.7 eV.[19] This is nicely confirmed by the experimental absorption edge value of 3.7 eV in MnO and 3 eV in CoO.[18]

For NiO and MnO the crystal-field parameter has been measured experimentally; $\Delta_{NiO} = 1.10$

eV,[20] and $\Delta_{MnO} = 1.25$ eV,[21] which makes a more detailed comparison between these two oxides possible. The difference in the crystal-field effect between NiO and MnO will therefore be $0.4 \times 1.10 + 0.6 \times 1.25 \approx 1.2$ eV. The difference in the $M^{2+}(d^n \rightarrow d^{n-1}s)$ excitation energy between manganese and nickel is 1.10 eV.[16] Thus, the similarity of the absorption edge in MnO and NiO is totally understandable as a crystal-field effect on the $d^n \rightarrow d^{n-1}s$ excitation energy.

Since the crystal field will be somewhat larger for the earlier hypothetical insulating monoxides than for the heavier ones, the derived values for the position of their absorption edge will actually constitute a lower limit. From this we can conclude that even for insulating TiO and VO the $d^n \rightarrow d^{n-1}s$ energy separation will be quite appreciable. Therefore, neither the mixed-valence idea nor the idea about a metallic d state due to a slight occupation of the s band seems to be appropriate for TiO and VO. Instead the d state forms a metallic state by itself and the physical situation is therefore quite close to the degenerate Hubbard model.[13]

III. METALLIC BINDING IN TiO AND VO AND STABILITY OF THE MONOXIDES

The experimental heat of formation of a compound refers to the standard state of the participating elements at 298 K. Here we will instead use the heat of formation relative to free atomic species. Since we are going to consider only oxides, the atomization energy of oxygen can be regarded as a redundant constant (which we in the following will put equal to zero). On the other hand, the cohesive energy of the metals[22] must be included. Further, having the divalent monoxides in mind, we atomize the metals to the $d^n s^2$ atomic configuration. In the formation of insulating oxides from free atoms:

$$M(d^n s^2 - \text{atom}) + \tfrac{1}{2}O_2 \rightarrow MO \quad (\Delta H_{\text{atom}}^{\text{II}}), \qquad (3.1)$$
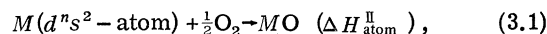
we would therefore expect a smooth behavior of the corresponding heat of formation $\Delta H_{\text{atom}}^{\text{II}}$ throughout the series. In Fig. 3 we show the experimental value for $\Delta H_{\text{atom}}^{\text{II}}$ for the $3d$ monoxides. As can be seen the behavior of $\Delta H_{\text{atom}}^{\text{II}}$ is far from regular, and instead TiO and VO are remarkably anomalous. Due to the ligand, there is, however, one complication in the bonding properties, namely, the influence of the ligand on the five d orbitals, which in the free atom are degenerate. To get an idea about the normal behavior of divalent insulating transition-metal compounds we consider $\Delta H_{\text{atom}}^{\text{II}}$ for the dihalides. In Fig. 4 we have plotted $\Delta H_{\text{atom}}^{\text{II}}$ for the dihalides relative to the value for the cor-
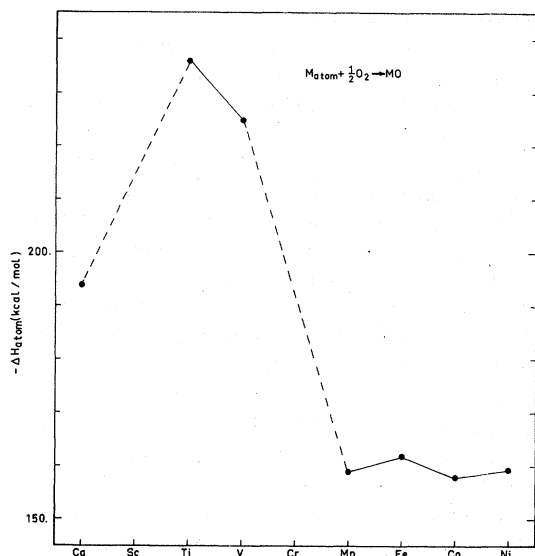
FIG. 3. Experimental values of $-\Delta H_{atom}^{II}$ [as defined in the text in connection with Eq. (3.1)] for the $3d$ monoxides. The experimental values are obtained from Refs. 22 and 23.

responding calciumdihalide. The close resemblance between the curves for the different halides is thereby clearly seen. In this figure we have also included the behavior of ΔH_{atom}^{II} for the heavier $3d$ monoxides. From the found general pattern it then becomes possible to derive ΔH_{atom}^{II} for the hypothetical insulating monoxides of the lighter $3d$ elements.

For the d^0, d^5, and d^{10} configuration, the ligand field stabilization energy is zero. A smooth interpolation in $-\Delta H_{atom}^{II}$ for the monoxides of Ca, Mn, and Zn would therefore give the heat of formation for the other monoxides in the case of zero ligand field splitting. The excess, derived from Fig. 4, of about 28 kcal/mol for NiO would then correspond to the ligand field effect on the d^8 orbital. This energy is equal to $\frac{6}{5}\Delta$. Thus, from this we derive that $\Delta_{NiO} = 1$ eV, which compares favorably with the experimental value: 1.1 eV.[20] Similarly, we find in the case of FeO, $\Delta_{FeO} = 1.2$ eV. This agrees with the expected trend of an increasing crystal-field splitting for the lighter $3d$ monoxides, and could be compared with the experimental value for MnO: $\Delta_{MnO}^{expt} = 1.25$ eV.[21]

As mentioned above, we could from Fig. 4 derive ΔH_{atom}^{II} for the hypothetical insulating monoxides. In Fig. 5 we compare the experimental values for TiO and VO with the derived ones. From this we can conclude that the experimental value of $-\Delta H_{atom}^{II}$ (TiO) exceeds the expected value by about 35 kcal/mol and the same difference for VO is about 25 kcal/mol. This large extra contribution to the

binding obviously has its origin in the *metallic nature* of the d state for these two compounds.

The characteristic feature of the transition-metal chemistry is the possibility of a variable oxidation state. This means in particular that the $3d$ monoxides may decompose into higher oxides, as, for example, the sesquioxides. It is therefore of interest to investigate this possibility in some detail, i.e., look for whether the following reaction

$$MO \rightarrow \tfrac{2}{3}MO_{3/2} + \tfrac{1}{3}M(\text{metal}),   (3.2)$$
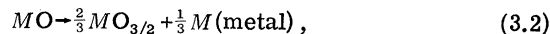
can occur spontaneously or not. In Fig. 5 we have included the heat of formation of the right-hand part of Eq. (3.2) from atomic $d^n s^2$ species. From this figure, several interesting conclusions can be drawn. First of all, in case TiO and VO could form the insulating compound, they would immediately decay into the higher oxide and the metal. Thus, it is only due to the metallic nature of
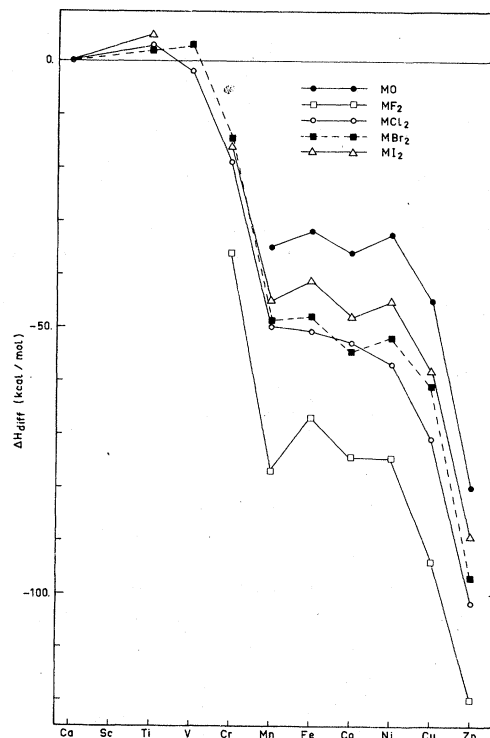

FIG. 4. Heat of formation relative to the atomic $d^n s^2$ configuration for the dihalides of the $3d$ elements. The monoxides are also included. For each dihalide the corresponding heat of formation ΔH_{atom}^{II} of the calcium dihalide has been put equal to zero. This has also been made for the monoxides. Therefore, the plot actually shows the difference ΔH_{diff} in the heat of formation between a $3d$ dihalide (monoxide) and its corresponding calcium dihalide (monoxide). The experimental values are taken from Refs. 23 and 24.
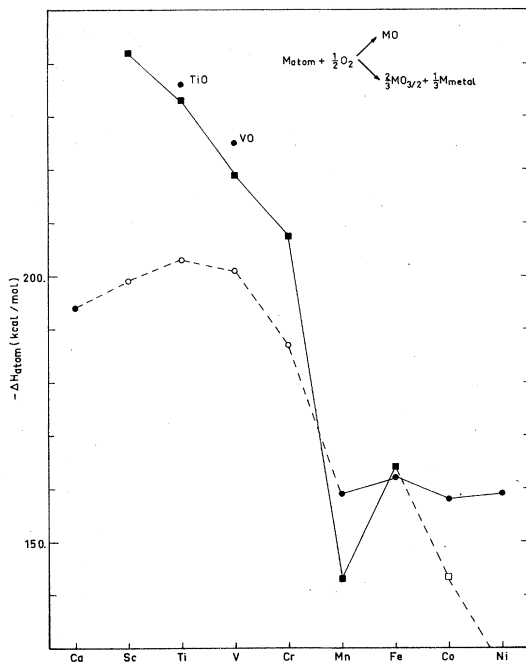
FIG. 5. Heat of formation $-\Delta H^{II}_{atom}$ for the reactions $M(d^n s^2 \text{ atom}) + \frac{1}{2}O_2 \to MO$ and $M(d^n s^2 \text{ atom}) + \frac{1}{2}O_2 \to \frac{2}{3}MO_{3/2} + \frac{1}{3}M_{metal}$, where M is a $3d$ element. Circles refer to monoxide and squares to sesquioxide and metal. The filled circles and filled squares correspond to experimental values (Refs. 22-24). The open circles and the open square are derived values for hypothetical insulating compounds. The open circles for insulating TiO and VO are below the corresponding filled squares, which means that they are highly unstable versus decomposition to the sesquioxide and the metal.

the d state, that these two monoxides exist. Even so, as can be seen from Fig. 6, they are very close to decomposition. This circumstance must be directly related to that both TiO and VO form over wide ranges of stoichiometry [$VO_{0.80}$ to $VO_{1.20}$ (Ref. 25)]. Even when prepared stoichiometrically, these two materials still contain about 15% vacancies on both the metal and oxygen sublattices.[26] In fact it is quite difficult to experimentally avoid that VO forms regions of pure vanadium alternating with regions of composition V_2O_3.

From Fig. 5 we notice that the only possibility for ScO to be stable against decomposition is by a metallic d binding of at least 45 kcal/mol. Studies on rare-earth chalcogenides indicate that a d-band contribution to the binding in the monoxides should be quite close to this value.[27] Therefore, ScO must be very close to existence. It should be stressed that this possibility only exists for an itinerant d state.

Also CrO is of interest. Again, as is evident from Fig. 5, an insulating compound would im-

mediately decay to the sesquioxide and pure metal. From the discernible trend in the metallic binding contribution <45, 35, and 25 kcal/mol for ScO, TiO, and VO, respectively, one might extrapolate that in hypothetical metallic CrO the d-band contribution would be about 15 kcal/mol. From Fig. 5 we note that this would mean that this hypothetical state is rather close to stability. However, as far as we are aware about, the chromium monoxide has not been experimentally identified.

The decreasing trend from ScO to CrO of the d-band contribution to the binding together with the large stability of the $3d^5$ atomic configuration makes it most reasonable that MnO is found to be an insulator. Therefore, the transition line between a metallic behavior and an insulating one is located somewhere between chromium and manganese monoxide (regarding Z as a continuous number). At the same time, however, for manganese the increased atomic d-correlation also leads to an increased value of the third ionization potential, and therefore the heat of formation of the sesquioxide is correspondingly affected. This fact guarantees that insulating manganese (II) oxide is stable against decomposition (see Fig. 5).
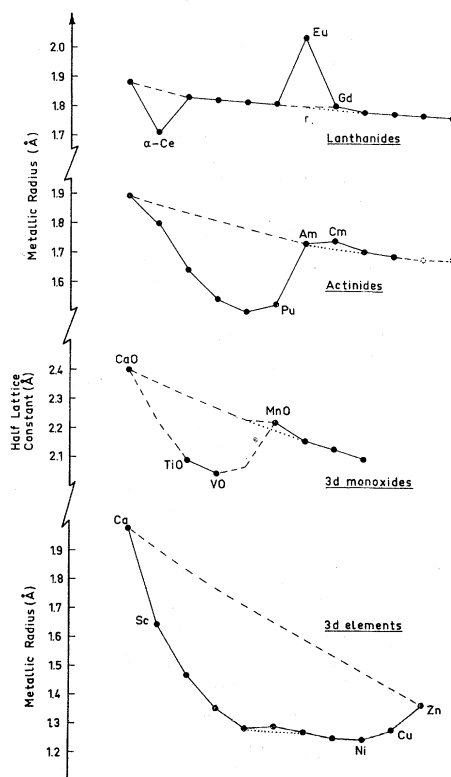

FIG. 6. Metallic radius for the lanthanides, actinides, and the $3d$ transition elements. For the $3d$ monoxides half the lattice constant is plotted.

For iron, the third ionization potential is decreased in comparison with manganese (compare with Fig. 2), and the formation of the iron (III) oxide is considerably facilitated. From Fig. 5 we note that this in fact implies that FeO is on the borderline for a decomposition to the higher oxide and the metal. This explains that stoichiometric FeO does not appear to exist, the stable form always lacks some iron and has a composition $Fe_{0.95}O$.

The following monoxide in the series CoO is again stable against a decay to the higher oxidation state, Fig. 5. The same holds true also for NiO and CuO.

In the 4*d* series, NbO appears to be the only existing monoxide for the lighter elements. For this material a similar procedure as for the 3*d* monoxides can be used to derive the ΔH_{atom}^{II} value for the hypothetical insulating oxide. Thereby one finds that $\Delta H_{atom}^{II} \simeq -230$ kcal/mol. The experimental value, however, is about -276 kcal/mol.[23] Again we are led to conclude that the *d* state is metallic and contributes to the binding by about 45–50 kcal/mol. This increased binding ability of the *d* state in NbO in comparison to VO, conforms to the general picture of the property of a 4*d* state relative to a 3*d* state.

The stability of NbO versus decay to higher oxides can be studied from the reaction

$$NbO \rightarrow \tfrac{1}{2} NbO_2 + \tfrac{1}{2} Nb_{metal} \qquad (3.3)$$

(Nb_2O_3 does not appear to exist). The enthalpy change for this reaction is found to be only about $+3$ kcal/mol. This means that NbO is stable, but close to an instability.

If some of the other earlier 4*d* element monoxides existed, they would certainly be metallic. However, due to the decreased binding of 4*d* electrons relative to 3*d* electrons in the earlier elements (Fig. 2), these elements readily form higher oxides, which are energetically favored over the monoxides. Only for NbO the conditions are so balanced that the extra binding due to the metallic *d* electrons overcomes the tendencies towards decomposition. For the heavier 4*d* elements only RhO and PdO have been reported. In the 5*d* series no stable monoxides are known (PtO is known only in solid solutions with platinum). These general trends in the existence of *d*-element monoxides are reflected in the $M^{2+}(d^n) \rightarrow M^{2+}(d^{n-1}s)$ excitation energies plotted in Fig. 2. To recapitulate, if, for the earlier elements in the 3*d* series, the monoxide compound existed, this was accidental and due to a metallic *d* state. Further, FeO was on the borderline of existence. Then, by comparing the $d^n \rightarrow d^{n-1}s$ excitation energy of the 4*d* and 5*d* series with those of the 3*d* series, it becomes quite un-

derstandable that only RhO, PdO, and AgO will be stable against higher oxidation numbers. (That AgO in itself might not exist is quite a different matter.)

IV. COMPARISON OF THE 3*d* MONOXIDES WITH OTHER SERIES OF ELEMENTS

The increased binding properties due to the metallic *d* state in TiO and VO is directly reflected by an anomalously small lattice parameter in comparison to the other monoxides, Fig. 6. In fact the volume is reduced by about 25% from the hypothetical volume of the insulating phase. This difference in volume is of similar nature as the volume change which takes place in a vapor-liquid phase transition of metallic atoms.

In Fig. 6 we have also plotted the metallic radius of the 3*d* metals. For these metals the *d* state is metallic throughout the whole series. This is obviously reflected in the interatomic distance. Therefore, this behavior is not directly comparable to the one found for the 3*d* monoxides. However, in the Periodic Table there is another series of elements which is more enlightening in this respect, namely, the actinides. The analogy of this series to the lanthanides might lead one to expect a similar smooth behavior of the metallic radius through the series as found for the trivalent rare-earth metals. However, since the 5*f* orbitals are more extended than the 4*f* orbitals, they form itinerant *f* states in the earlier elements of the series. Thus the 5*f* electrons are metallic in the lighter actinides, but localized in americium and the heavier elements.[28-31] In Fig. 6 we have included the metallic radius of the actinides. As can be seen, its behavior is remarkably similar to the one for the 3*d* monoxides. The only case which is somewhat misleading in this respect is thorium, which is a tetravalent metal with no occupation of the 5*f* band. Most clear-cut examples for a comparison with the 3*d* monoxides are neptunium and plutonium, which, were it not for the itinerant *f* electrons, should be normal trivalent rare-earth-like metals. As can be seen from Fig. 6, the volume decrease due to the metallic *f* electrons is about 30%, which is directly comparable with the corresponding volume decrease for the metallic 3*d* monoxides. Further, uranium and most probably protactinium are superconductors.[30,32] In this respect TiO is the analog compound among the 3*d* monoxides, becoming a superconductor at 1.3 K.[33]

In uranium the contribution of the metallic 5*f* electrons to the binding energy has been shown to be about 30 kcal/mol.[31,34] For neptunium the metallic *f* contribution is somewhat less and in plu-

tonium it is about 15–20 kcal/mol.[31,34] Again, this behavior is indeed comparable to the one for the $3d$ monoxides.

Even among the $4f$ elements, there is a similarity to the $3d$ monoxides. What we have in mind is the γ-α transition in cerium, which is due to a phase transformation from a localized to an itinerant behavior of the $4f$ electron.[35] Thus cerium corresponds to the borderline between metallic and insulating behavior among the $3d$ monoxides, and should therefore be most similar to CrO. Highly compressed cerium is a superconductor[36] which would correspond to TiO. The similarity in the behavior of the metallic radius between the lanthanides and the $3d$ monoxides can also be seen in Fig. 6.

V. DISCUSSION

The $3d$ monoxides provide an excellent opportunity to study how an itinerant behavior changes into a localized one. From this series of compounds we may therefore derive the most salient features which should characterize and accompany such a transition.

In the present paper we have focused our attention to two bulk properties, the binding energy and the lattice constant. It was found that both of them are dramatically dependent on the nature of the $3d$ state. The extra contribution to the binding due to the metallic d electrons was found to decrease monotonically in the series ScO, TiO, VO, and CrO. From this trend, the localized behavior found in the heavier $3d$ monoxides can be rationalized. Accompanying this localization, there is a pronounced change in the lattice constant. Therefore, highly relevant experiments would be high-pressure studies of the insulating oxides. However, even though pressures up to about 400–500 kbar have been applied to these materials, no transition to a metallic state was observed.[37] Thereby it should be noticed that the present monoxides are highly incompressible, while the corresponding lattice constant decrease at these high pressures is only about 5%. This may explain the difficulties to metallize the monoxides by compression. Still, NiO has been claimed to undergo an insulator-metal transition above 2 Mbar.[38] However,

this experimental result, obtained at such extraordinarily high pressures, needs to be confirmed.

An amusing circumstance, which was found in Sec. III, was that the hypothetical insulating lighter $3d$ monoxides should immediately decompose into the pure metal and the sesquioxide. Therefore, it is only the metallic property which guarantees that TiO and VO exist as stable compounds. *Thus, their very existence is a demonstration of a metallic d state.*

Obviously, an experimental study of the mixed compounds $Ti_{1-x}Mn_x O$ and $V_{1-x}Mn_x O$ should be of considerable interest for a more detailed study of the insulator-metal transition. However, it might be that these types of alloy compounds are impossible to prepare as homogeneous systems, due to decomposition processes towards higher oxidation states. By this we touch on the fundamental experimental difficulties involved in the studies of the $3d$ monoxides, namely, the problem associated with the preparation of stoichiometrically well-defined, defect- and impurity-free compounds.

From the experimental energy of the $d^n \to d^{n-1}s$ excitation in the free divalent ions and the experimental position of the absorption edge in NiO, it became possible to derive the position of the absorption edge of the other insulating monoxides. By an explicit consideration of the ligand field splitting of the d level, the experimental absorption edge in MnO could then be accounted for. Further, it was found that even in TiO and VO the separation between the d state and the s band is too large for permittance of an occupation of the latter. Therefore, the delocalization of the d state exclusively takes place within the d state itself.

We believe that the comparison, given in Sec. IV, between the $3d$ monoxide series and the actinide series can give additional insight into the behavior of both of them. Of course, one important difference is that in the actinides the intra-atomic $5f$ correlation is heavily screened by the other metallic electrons in the (sd) band. The presence of these (sd) electrons also means that in the actinides there is no corresponding drastic change in the electrical conductivity properties as among the $3d$ monoxides. On the other hand, the magnetic behavior should be more appropriate for a direct comparison.

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