Mössbauer Study of Ruthenium Borides and Phosphides

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The Mössbauer absorption of the 89-keV gamma rays of ^{99}Ru has been used in a study of a series of ruthenium borides and phosphides. The results are compared with Mössbauer data for the corresponding iron compound. The Mössbauer parameters of the transition metal atom in the borides turn out to be rather insensitive to the detailed boron surrounding. The results for the phosphides suggest similar electron configurations for the iron and corresponding ruthenium compounds.

Introduction

The crystal chemistry of borides and phosphides has been extensively studied by the Uppsala School (*1*). In these investigations, several ruthenium compounds with boron and phosphorus have been prepared and crystallographically characterized. Information on the chemical bonding in these compounds being still scarce, it was thought worthwhile to study them by the Mössbauer method. The 89-keV state in ^{99}Ru is well suited for this purpose, and it is of interest to compare the experimental results with those found (*2, 3*) for various other Ru compounds. Moreover, since ruthenium has the same number of electrons outside the noble gas core as iron, it is interesting to compare results for the borides and phosphides of ruthenium with the Mössbauer parameters of the corresponding iron compounds (*4, 5*).

Crystallographic Data

Borides with the nominal compositions $RuB_{\sim1.1}$, $RuB_{\sim1.5}$, and $RuB_{\sim2.1}$ were studied by Aronsson et al. (*6, 7*) and by Lundström (*8*). The ideal compositions were shown to be RuB (with the hexagonal WC structure), Ru_2B_3 (with the hexagonal W_2B_5 structure), and RuB_2

(with orthorhombic structure, space group *Pmmn*). In all these compounds, the ruthenium atoms occupy only one crystallographic position.

The phosphides Ru_2P, RuP, and RuP_2 have been discussed by Rundqvist (*9*). They are all orthorhombic with the anti-$PbCl_2$ structure (Ru_2P), the MnP structure (RuP), and the FeS_2 marcasite structure (RuP_2). In Ru_2P, there are two inequivalent crystallographic positions for ruthenium which are populated by equal numbers of Ru atoms.

Experimental Details

The samples used in the present investigation were the ones used in the original crystallographic studies. They were kindly supplied by Prof. Rundqvist and Dr. Lundström. The transmission Mössbauer spectra (Figs. 1 and 2) were recorded with both the source of ^{99}Rh in Ru metal and the absorber cooled to 4.2°K. Further details of the experimental method and the data analysis have been given previously (*2, 3*). To all spectra except those of RuB_2 and Ru_2P, a superposition of two Lorentzian lines of equal width and intensity has been least-squares fitted. Since the electric quadrupole splitting of the $(5/2)^+$ ground state is too small to be resolved in any of the spectra, the doublet separation thus obtained is virtually identical with the splitting $\Delta E_Q = (1/2)e^2qQ_{3/2}$ $(1 + \eta^2/3)^{1/2}$ of the $(3/2)^+$ first excited state of

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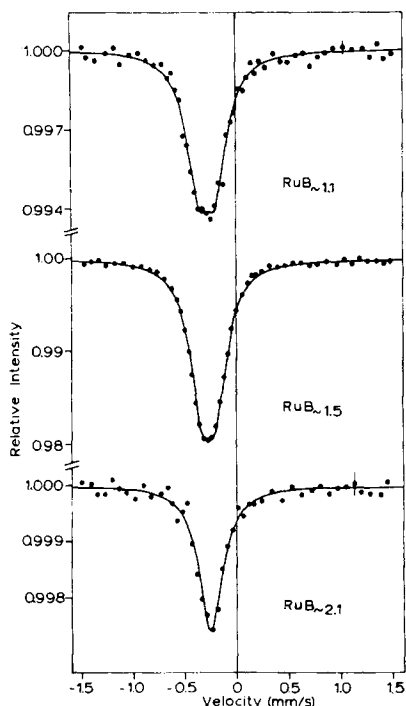† Correspondence should be mailed to this address.

FIG. 1. Mössbauer spectra of ruthenium boride absorbers taken with a source of ^{99}Ru metal.
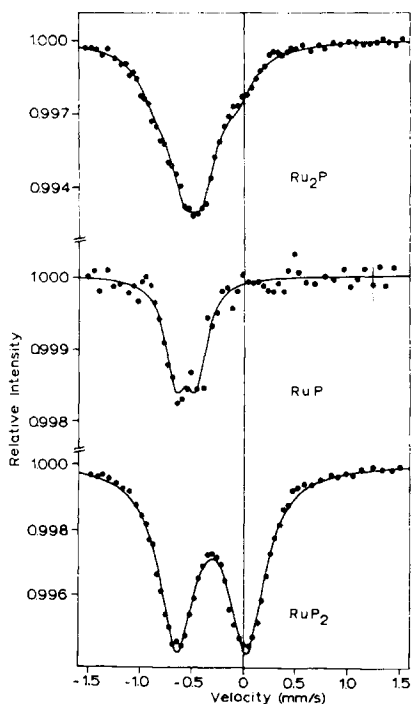

FIG. 2. Mössbauer spectra of ruthenium phosphide absorbers taken with a source of ^{99}Ru in Ru metal. The Doppler velocity is given in mm/sec.

^{99}Ru, where eq and η are the z component and assymetry parameter of the electric field gradient at the ruthenium nuclei and $Q_{3/2}$ is the quadrupole moment of the 89-keV state of ^{99}Ru.

The $RuB_{\sim 2.1}$ spectrum shows no indication of a quadrupole splitting and was fitted with a single Lorentzian line. In the Ru_2P spectrum, the two different crystallographic positions for the Ru atoms give rise to two quadrupolets which are badly resolved. Although the two sites have the same Ru occupancies, one cannot a priori assume that the two quadrupole patterns have the same intensity, since the recoilless fractions may be, and according to X-ray data (9) indeed should be, different for the two positions. Considering this we could not obtain an unambiguous interpretation of the spectrum and give only a value for the centre-of-gravity shift of the whole pattern.

Results and Discussions

The numerical results are summarized in Table I. In order to facilitate a comparison of the isomer shifts found in the present study with those obtained previously for the corresponding iron compounds, the appropriate values have been compiled in Fig. 3. The scales on which the ^{57}Fe and ^{99}Ru isomer shifts have been plotted were adjusted in such a way that isoelectronic compounds of Fe and Ru can be connected by horizontal lines. This amounts to an elimination of the nuclear factor $\delta\langle r^2 \rangle$ in the comparison of isomer shifts of the two elements. The applicability of this method for transition elements in general will be discussed in detail in a forthcoming paper (10).

The isomer shifts obtained for the ruthenium borides are all nearly the same with a slight increase in s-electron density with increasing number of boron neighbours. This is analogous to the iron case, where the difference between the values for FeB and Fe_2B (4) is also rather small (see Fig. 3). In the metal-rich iron borides, the quadrupole splitting is small for all iron–boron ratios (4). In the ruthenium borides, the splitting is also relatively small and decreases with decreasing ruthenium content (Table I). The transition metal electron configuration thus seems to be rather insensitive to the exact boron surrounding. This agrees with the idea brought forth by Kiessling (1, 11), that the transition-metal borides have rather weak interactions between the boron atoms and the transition metal atoms.

TABLE I

SUMMARY OF THE EXPERIMENTAL RESULTS[a]

Compound	IS	ΔE_Q	W	t
$RuB_{1.1}$	-0.28 ± 0.01	0.17 ± 0.0	0.26 ± 0.02	170
$RuB_{1.5}$	-0.27 ± 0.01	0.15 ± 0.0	0.26 ± 0.02	250
$RuB_{2.1}$	-0.25 ± 0.01	—	0.28 ± 0.02	260
Ru_2P^b	-0.48 ± 0.04			280
RuP	-0.56 ± 0.02	0.20 ± 0.03	0.24 ± 0.04	265
RuP_2	-0.30 ± 0.01	0.68 ± 0.01	0.40 ± 0.02	240

[a] The isomer shifts (IS) relative to Ru metal, the quadrupole splitting $\Delta E_Q = (1/2)e^2qQ_{3/2}(1 + \eta^2/3)^{1/2}$, and the FWHM line width W are all given in mm/sec. The absorber thickness t is given in mg/cm² of natural ruthenium.

[b] For Ru_2P only, the average over the two different crystallographic positions is given for the isomer shift. The quadrupole splittings and linewidths for the two sites could not be determined unambiguously.

For the phosphides, a substantial variation of the Mössbauer parameters with composition is found (Table I). The electric quadrupole splitting in RuP_2 is, in fact, the largest found so far for
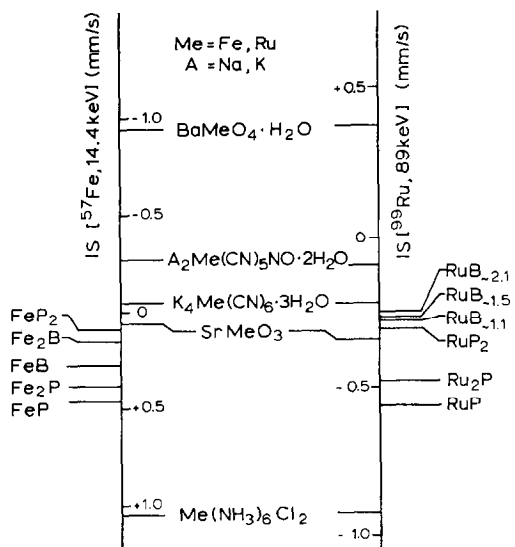

FIG. 3. Comparison of the isomer shifts IS for the borides and phosphides of Ru with room-temperature values previously obtained [4, 5] for the corresponding iron compounds. The shifts for Fe_2P and Ru_2P are averages over the two different crystallographic positions. The scales on which the shifts are plotted have been chosen in such a way that horizontal lines connect isoelectronic ruthenium and iron compounds. The isomer shifts of the isoelectronic compounds that have been used to adjust the scales are plotted in the central column of the figure. These data have been taken from Refs. 2, 3, 14, and 16.

Ru compounds. This is similar to the exceptionally large quadrupole interaction that has recently (12) been found in OsP_2. In comparing the results for Ru_2P with those obtained earlier for Fe_2P, one has to take into account that Fe_2P and Ru_2P have different crystal structures (5).

The Mössbauer parameters for iron in $Ru_{2-x}Fe_xP$ and $Co_{2-x}Fe_xP$, both of which have the orthorhombic anti-$PbCl_2$ structure of Ru_2P, do not, however, deviate drastically from those obtained for the hexagonal Fe_2P structure (5).

As has been mentioned earlier, the Mössbauer spectrum of Ru_2P cannot be reliably decomposed. The spectrum (Fig. 2) shows an asymmetry resulting from the two crystallographic positions for Ru. The centre-of-gravity shift for Ru_2P, however, falls close to corresponding points for Fe_2P (5) on the isomer shift plot (Fig. 3). A similar situation is found for the isomer shifts of RuP and RuP_2. Furthermore, the ratio between the quadrupole splittings in the mono- and diphosphides is close to 3 in the iron as well as in the ruthenium case (Table I and Ref. 5).

With the exception of RuP_2, all the compounds studied in the present work are believed to be electric conductors, while RuP_2 is a diamagnetic semiconductor with a bandgap of about 1 eV (1). Since the conduction band of RuP_2 should be empty at 4.2°K, the compound can be treated as an insulator at that temperature. Hulliger (13) has described the crystal-chemical, electric, and magnetic properties of the marcasites in terms of localized d electrons. In this model, RuP_2 may be considered as being made up of Ru^{4+} and $(P_2)^{4-}$ ions. The strongly deformed octa-

hedral surrounding of the transition metal causes splitting of the t_{2g} orbitals into a low-lying doublet, forming the valence band in the solid, and a singlet giving rise to the conduction band. The bandgap is a direct measure of the splitting. The isomer shift of RuP_2, being nearly the same as the shifts for $SrRuO_3$ (14), RuO_2, and K_2RuCl_6 (2), confirms the expectation of tetravalent Ru with a $4d^4$ electron configuration for RuP_2. A d^4 configuration has also been assigned to iron in FeP_2 on the basis of the Mössbauer isomer shift. Goodenough (15) has recently discussed the similarities between marcasites containing Fe, Ru, and Os, and a Mössbauer study to further substantiate these views is currently being made.

Conclusions

The present investigation has shown that the metal ion in the ruthenium borides is rather insensitive to the boron surrounding. The electron configurations of iron and ruthenium borides, seem, however, to be closely similar.

In the phosphides, the analogy between the crystal structures for iron and ruthenium compounds is paralleled by a similarity of the electron configurations. The isomer shift for RuP_2 is in agreement with the notion of a $Ru^{4+} (P_2)^{4-}$ ionic formula (13) for RuP_2.

Acknowledgments

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