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NOTE

^{99}Ru Mössbauer Spectroscopic Evidence for the Presence of Discrete Ruthenium(III) and Ruthenium(IV) Ions in the Compounds $Ba_4Ru_3NbO_{12}$ and $Ba_4Ru_3TaO_{12}$

A special feature of the ternary and quaternary oxides of ruthenium is their propensity to adopt structures containing clusters of ruthenium ions isolated from one another in three-dimensional lattices. Examples include: (a) the phases of general formula $Ba_3Ru_2MO_9$, which crystallize with the hexagonal barium titanate-type structure and contain ruthenium(V) in dimeric $(Ru_2O_9)^{8-}$ clusters (*1, 2*); (b) the compound $BaRuO_3$, which adopts the nine-layer hexagonal structure and contains ruthenium(IV) in $(Ru_3O_{12})^{12-}$ clusters (*3*); and (c) the ordered NaCl-type phase Na_3RuO_4 which features ruthenium(V) in $(Ru_4O_{16})^{12-}$ clusters (*4, 5*). The magnetic exchange interactions in such systems are of considerable interest, and have recently been studied in some depth, both by magnetic susceptibility measurements (*2, 6*) and, in our own laboratory, by ^{99}Ru Mössbauer spectroscopy (*7–9*). Recently, Darriet and co-workers have synthesized the new phases $Ba_4Ru_3MO_{12}$ (M = Nb or Ta) which are isomorphous with Ba_2NiTeO_6 and are thought to contain $(Ru_3O_{12})^{13-}$ clusters isolated magnetically from one another by corner-shared MO_6 octahedra, as shown in Fig. 1 (J. Darriet and M. Drillon, private communication). These phases show magnetic susceptibility data characteristic of isolated trimers but, unlike the compounds mentioned earlier, contain ruthenium in mixed oxidation states. If the *d* electrons are considered to be localized at each ruthenium site, then two arrangements are possible, namely, Ru^{IV}–Ru^{III}–Ru^{IV}, which conserves the local elements of symmetry of the structure, or Ru^{IV}–Ru^{IV}–Ru^{III}. An alternative possibility is that there is substantial delocalization leading to charge averaging. ^{99}Ru Mössbauer spectroscopy could, in principle, provide evidence to distinguish between these possibilities.

The Mössbauer spectra were recorded at 4.2 K with both the source and absorber immersed in liquid helium, using apparatus described previously (*10*). The source was a

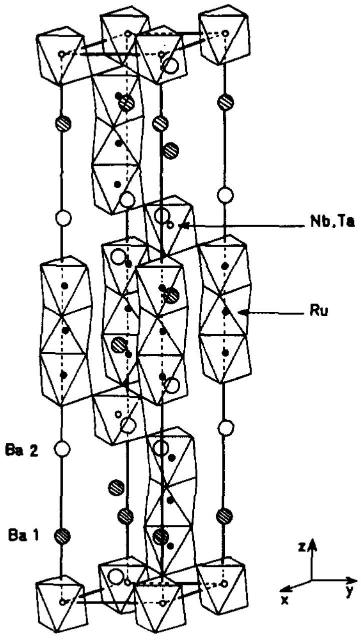

FIG. 1. Crystal structure of the phases $Ba_4Ru_3MO_{12}$ (M = Nb, Ta).

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nominal 5 mCi of ^{99}Rh in a matrix of ruthenium metal and the absorbers contained ~400 mg cm^{-2} of compound, kindly supplied by Dr. J. Darriet. The ^{99}Ru chemical isomer shift data are quoted relative to an absorber of natural ruthenium metal at 4.2 K and of thickness 140 mg cm^{-2}; the experimental linewidth of the 90-keV resonance obtained with this absorber was found to be 0.25 ± 0.01 mm sec^{-1}.

The spectrum for $Ba_4Ru_3TaO_{12}$ is shown in Fig. 2 and that for the analogous niobium compound was very similar. Each consists of a broad asymmetric resonance with a distinct shoulder on the high-velocity side of the profile, suggesting the presence of at least two separate components. There is no indication of magnetic hyperfine splitting in either of the spectra, which immediately rules out the possibility of long-range magnetic ordering in these phases.

The simplest analysis would involve fitting the spectra with two lines, and on a purely visual basis this would yield components at ca. −0.43 and −0.24 mm sec^{-1} with intensities in the approximate ratio 2:1. Previous work on oxide phases in this laboratory has established that Ru^{IV} resonances appear in the range −0.23 to −0.33 mm sec^{-1} (*8*), whereas Ru^{III} resonances occur at more negative velocity, the only definitive examples being $LaRuO_3$ (*11*) and Co_2RuO_4 (*12*) with values of −0.56 and −0.57 mm sec^{-1}, respectively. This over-simple analysis would therefore suggest that there are twice as many Ru^{III} as Ru^{IV} ions present, which is clearly inconsistent with the chemical formula. A more realistic analysis, in terms of three lines, is shown for the spectrum of $Ba_4Ru_3TaO_{12}$ in Fig. 2. The solid line through the data points represents the computed least-squares fit in an analysis in which the half-widths and intensities as well as the positions of the three components were free to vary. The lines are positioned at −0.52, −0.38, and −0.19 mm sec^{-1} and have relative areas of 0.8:1.0:0.7; their half-widths are 0.33, 0.30, and 0.33 mm sec^{-1}, respectively. This fit gave $\chi^2 = 213$ on 236 degrees of freedom, and a related fit in which the linewidths and intensities were constrained to be equal gave very similar values for the line positions and only a slight increase in the value of χ^2 (248 on 248 degrees of freedom). A similar constrained three-line fit to the spectrum of

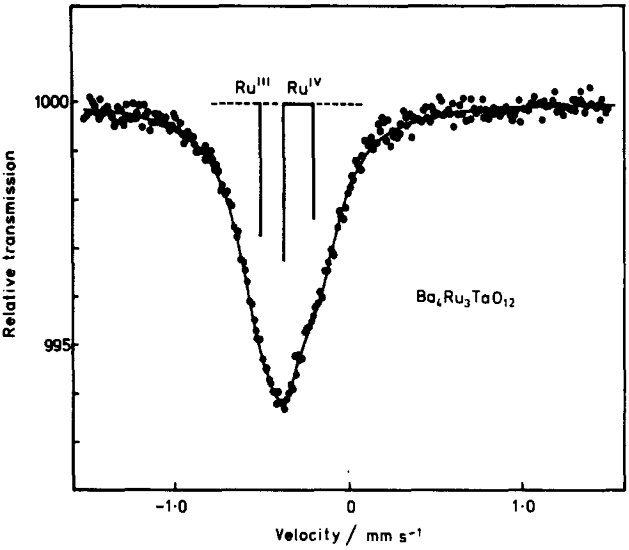

FIG. 2. ^{99}Ru Mössbauer spectrum at 4.2 K for $Ba_4Ru_3TaO_{12}$ showing a possible three-component fit. The computed value of the baseline is 35.97×10^6 counts.

$Ba_4Ru_3NbO_{12}$ gave lines at −0.45, −0.38, and −0.20 mm sec^{-1} with a half-width of 0.32 mm sec^{-1} and $\chi^2 = 357$ on 248 degrees of freedom. If the line at most negative Doppler velocity is assigned to Ru^{III} in each case and the other two lines to a quadrupole doublet from Ru^{IV}, then the relative proportions of the two oxidation states are consistent with the chemical formulation, which gives confidence in the analysis. It should be noted that quadrupole splitting of the ^{99}Ru resonance actually produces an overlapping six-line pattern but, because $Q_e/Q_g \sim 3$, this can be approximated by two sets of unresolved triplets for small values of the splitting (*12*), and there is nothing to be gained by attempting a more detailed analysis of the present spectra.

On this basis the Ru^{III} components have chemical isomer shifts of −0.52 and −0.45 mm sec^{-1}, respectively, for the Ta and Nb compounds, which are only slightly less negative than those for $LaRuO_3$ and Co_2RuO_4 given earlier; likewise the Ru^{IV} resonances have values of −0.29 mm sec^{-1} which are typical for this oxidation state. The absence of quadrupole splitting for the Ru^{III} resonances implies that there is very little distortion of the octahedral sites. A similar result was observed for the perovskite $LaRuO_3$ (*11*), whereas the trigonal field at the octahedral site in Co_2RuO_4 (*12*) produced a very large quadrupole splitting of the Ru^{III} resonance. The quadrupole splittings $|\frac{1}{2}e^2qQ_e| = 0.19$ mm sec^{-1} assigned to the Ru^{IV} components in the present compounds are small, but nevertheless imply that distortions exist at these sites.

It is interesting to recall that the two structurally nonequivalent ruthenium environments present in the nine-layer structure of $BaRuO_3$ are not distinguished in the Mössbauer spectrum of this compound, which consists of a sharp single line at −0.26 mm sec^{-1} (*8*). The trinuclear clusters in $Ba_4Ru_3MO_{12}$ are geometrically very similar to those in $BaRuO_3$ and it, therefore, seems reasonable to attribute the nonequivalence indicated in the present Mössbauer spectra to differences in the oxidation states of the individual ruthenium ions, as discussed above. However, it is clearly not possible to draw more detailed conclusions about the distributions of Ru^{III} and Ru^{IV} within the trinuclear clusters, except perhaps to comment that the relatively high value of χ^2 for the fit of the spectrum of $Ba_4Ru_3NbO_{12}$ could be a consequence of disorder between the Ru^{III} and Ru^{IV} ions within the clusters.

Throughout the discussion it has been assumed that the Nb and Ta are present in the +5 oxidation state, and the results are consistent with this assumption. However, the existence of substantial concentrations of Nb^{IV} and Ta^{IV} in the tetragonal-tungsten-bronze-like phases $M^I_2M^{II}_2Eu_2Nb_{10}O_{30}$ and $M^I_2M^{II}_2Eu_2Ta_{10}O_{30}$ has recently been inferred from their ^{151}Eu Mössbauer spectra (*13*), and their presence in small amounts cannot be entirely ruled out in the present compounds on the basis of the ^{99}Ru Mössbauer spectra alone.

In conclusion, we have shown that the ^{99}Ru Mössbauer spectra at 4.2 K for the phases $Ba_4Ru_3MO_{12}$ (M = Nb or Ta) can be interpreted in terms of the presence of discrete Ru^{III} and Ru^{IV} ions in an approximate ratio of 1:2. It would be interesting to apply the same technique to study the detailed electron distribution in several other recently prepared compounds which contain clusters of ruthenium ions with mixed oxidation states, notably, $La_3Ru_3O_{11}$(*14, 15*), $La_4Ru_6O_{19}$ (*16*), $La_8Ru_4O_{21}$ (*17*), and $Bi_3Ru_3O_{11}$ (*18*).

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