

## Magnetic Hyperfine Splitting of the $^{99}\text{Ru}$ Mössbauer Resonance in $\text{SrRuO}_3$

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**Summary** The  $^{99}\text{Ru}$  Mössbauer spectrum of  $\text{SrRuO}_3$  at 4.2 K shows a magnetic hyperfine splitting; the internal field of 352 kG at 4.2 K (315 kG at 77 K) is shown to be compatible with the ferromagnetic moment derived from neutron diffraction data, and confirms the collective-electron magnetism model for this compound.

THE occurrence of chemical isomer shifts in the 90 keV  $^{99}\text{Ru}$  Mössbauer resonance and the presence in some instances of quadrupole splittings have recently been documented by several groups for about fifty ruthenium compounds with nominal oxidation states ranging from +2 to +8 inclusive.<sup>1-4</sup> However, none of these compounds shows magnetic ordering even at 4.2 K, and resolved magnetic hyperfine splitting of the  $^{99}\text{Ru}$  resonance has only been previously reported for an alloy of 2.3 atom % ruthenium in metallic iron.<sup>5</sup> Other related work on the measurement of hyperfine fields has concerned  $^{99}\text{Ru}$  perturbed-angular-correlation studies in iron and nickel,<sup>6</sup> and  $^{101}\text{Ru}$  spin-echo n.m.r. in iron, cobalt, and nickel;<sup>7</sup> in all cases the ruthenium has been an impurity in a magnetically concentrated metal.

We report here the first observation of a hyperfine magnetic field in a ruthenium compound,  $\text{SrRuO}_3$ . This oxide orders ferromagnetically below 160 K;<sup>8</sup> it shows a collective-electron magnetism and metallic properties,<sup>8</sup> resulting in characteristic behaviour in the electrical resistivity<sup>9</sup> and the pressure dependence of the Curie temperature.<sup>10</sup> Some doubt exists as to whether the phase can be oxygen deficient.<sup>11,12</sup> The spontaneous ferromagnetic moment of  $1.4 \pm 0.4$  B.M., derived from neutron diffraction data at 4.2 K, is much lower than expected for a  $4d^4$  strong-ligand-field configuration with localised-electron magnetism.<sup>12</sup>

A sample of  $\text{SrRuO}_3$  was prepared and characterised using published data.<sup>11</sup> Mössbauer spectra were obtained with both source and absorber at either 77 K or 4.2 K using previously described techniques,<sup>4</sup> except that the source was prepared by a  $^{99}\text{Ru}(d,2n)^{99}\text{Rh}$  reaction on a pellet of natural ruthenium metal.<sup>1</sup> The spectrum at 4.2 K of an absorber containing  $1.27 \text{ g cm}^{-3}$  of  $\text{SrRuO}_3$  is shown in the Figure. The absorption dip is 0.16% with a total of  $122 \times 10^6$  counts per channel. The transition between the  $I_g = 3/2$  excited state and the  $I_g = 5/2$

ground state results in 18 magnetic hyperfine lines whose relative intensities are given by the Clebsch-Gordan coefficients for  $E2$  and  $M1$  transitions. The relative mixing ratio,  $\delta^2$ , is known to be  $2.7 \pm 0.6$  from Kistner's data;<sup>5</sup> the ratio of the nuclear magnetic moments,  $\mu_e/\mu_g$  is  $0.455 \pm 0.010$ ,<sup>5</sup> and  $\mu_e$  is  $-0.284 \pm 0.006 \mu_N$ , whence  $\mu_g$  is  $-0.623 \pm 0.019 \mu_N$ .<sup>13</sup> This latter value then gives the field at  $^{99}\text{Ru}$  in metallic iron at 4.2 K as  $-505 \pm 20$  kG. These parameters enable the interdependence of the component hyperfine lines to be established.

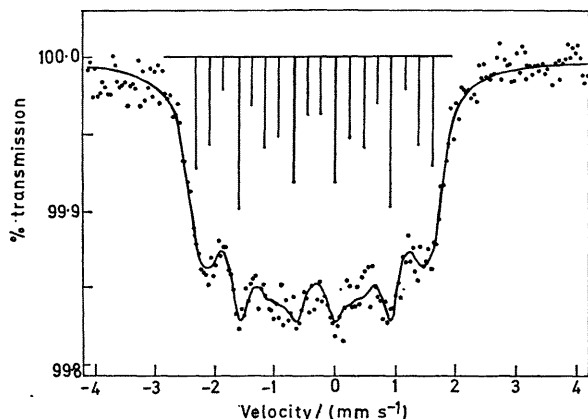


FIGURE. The  $^{99}\text{Ru}$  Mössbauer spectrum of  $\text{SrRuO}_3$  at 4.2 K.

The solid curve in the Figure is a computed least-squares fit with five variables: (a) the hyperfine magnetic field, (b) the chemical isomer shift relative to ruthenium metal, (c) the baseline, (d) a single value to scale the relative intensities, and (e) the linewidth. The component lines produced by the imposed constraints are shown as a bar diagram and the final fit has a chi-squared value of  $\chi^2 = 184$  on 194 degrees of freedom. The magnetic field is  $352 \pm 15$  kG at 4.2 K, with a chemical isomer shift of  $-0.325$

$\pm 0.007$  mm  $\text{s}^{-1}$  relative to ruthenium metal and a line-width of  $0.43 \pm 0.02$  mm  $\text{s}^{-1}$ ; corresponding values at 77 K are  $315 \pm 15$  kG,  $-0.305 \pm 0.021$  mm  $\text{s}^{-1}$ , and  $0.35 \pm 0.05$  mm  $\text{s}^{-1}$ . The sign of the field has not been determined but is assumed to be negative.

$\text{SrRuO}_3$  has a perovskite structure which is close to cubic.<sup>11</sup> Re-computation of the Mössbauer data with an axially symmetric quadrupole splitting of the excited state  $\frac{1}{2}e^2qQ_e$  parallel to the magnetic field (and neglecting any ground state splitting because  $Q_e/Q_g > 3$ ) gave a value for  $\frac{1}{2}e^2qQ_e$  of  $-0.010 \pm 0.006$  mm  $\text{s}^{-1}$  with  $\chi^2 = 181$ . We therefore consider the quadrupole splitting to be zero within experimental error.

Few data are available for magnetic hyperfine fields in the 4d-transition series. Calculations have shown that the Fermi core-polarisation term for a single unpaired 4d-electron will be ca.  $-370$  kG.<sup>6</sup> On this basis the observed field at 4.2 K corresponds to 1.0 unpaired electrons on the ruthenium, and may be compared with the values of  $1.4 \pm 0.4$  B.M. per mol from the neutron diffraction data, and 0.85 B.M. per mol at 77 K from the bulk magnetisation.<sup>9</sup> It is difficult to assess the role of any orbital contribution to the hyperfine field because the degree of anisotropy (if any) at the ruthenium is not known. However, assuming that this is small, our data are fully consistent with the reduced ferromagnetic moment of this compound.

Further analysis of the spectrum is not appropriate at present because of the lack of comparative data, but it is clear that  $^{99}\text{Ru}$  Mössbauer spectroscopy provides the basis for a detailed study of related magnetic ternary and quaternary ruthenium oxides; this has immediate relevance to an understanding of the magnetic properties of the 4d-transition series.

We thank the S.R.C. for financial support and a Studentship to P. K.

(Received, January 18th, 1971; Com. 092.)

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