

# NMR study of $A_2FeMO_6$ ( $A = Ca, Sr, Ba, M = Mo, Re$ ) double perovskites

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## Abstract

A nuclear magnetic resonance study of the  $A_2FeMO_6$  ( $A = Ba, Sr, Ca; M = Mo, Re$ ) double perovskites is reported. Spin echo spectra have been measured at 4.2 K and zero external magnetic field. Resonant signals at Mo nuclei are observed at 30–80 MHz and at 750–1000 MHz for Re nuclei. Frequencies of the main lines correspond to Mo hyperfine fields of 19, 24 and 23 T and to Re hyperfine fields of 84, 94 and 95 T for Ba, Sr and Ca compounds, respectively. From these data the values of Mo and Re magnetic moments are derived and the relation to the results of theoretical calculations is discussed.

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Perovskite compounds have recently attracted a great deal of interest in basic and applied research due to their extraordinary structural, magnetic and electronic properties. Among them are double perovskites of the formula  $A_2BB'O_6$  ( $A =$  alkaline earth or rare earth,  $B, B' =$  different transition metals) with an ordered  $B, B'$  cation alignment in the structure. Some of them, including Fe–Mo and Fe–Re compounds, exhibit half-metallic ferromagnetism (ferrimagnetism) with  $T_C$  higher than 400 K and a significant low-field magnetoresistance at room temperature [1]. The largest  $T_C$  was found for rhenium double perovskite [2]. Magnetic coupling and half-metallicity of the compounds are described by a

model which involves a conduction band consisting of overlapping spin down 3d, 2p and 4d(5d) bands of Fe, O and Mo(Re), respectively. It implies a non-vanishing 4d(5d) electron density and, correspondingly, non-zero magnetic moments of the 4d(5d) element. Recent neutron diffraction and nuclear magnetic resonance (NMR) measurements have proven the existence of a magnetic moment at the Mo site [2,3] in  $Sr_2FeMoO_6$ . In order to get the information on the magnetic moments at the Mo and Re sites in the compounds with different alkaline earth elements the present study has been undertaken.

NMR measurements has been carried out with a frequency swept spectrometer [4], at 4.2 K and at zero external magnetic field. The spin echo spectra have been obtained with two pulse sequence at pulse power adjusted to an optimum signal for each compound. Powder samples prepared by the solid-state reaction technique were measured. The spectra are shown in Figs. 1 and 2.

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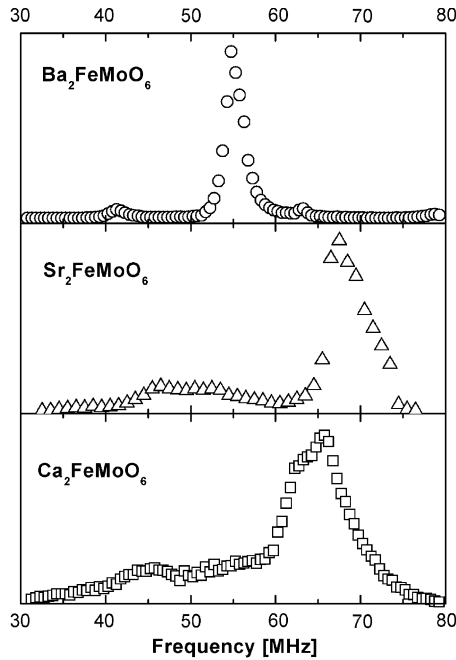


Fig. 1. <sup>95</sup>Mo and <sup>97</sup>Mo NMR spectra of A<sub>2</sub>FeMoO<sub>6</sub> compounds at 4.2 K and zero external magnetic field.

For the A<sub>2</sub>FeMoO<sub>6</sub> compounds, the resonant signal is observed in the range 30–80 MHz. Following our previous study [3], the signal is identified as originating from <sup>95</sup>Mo and <sup>97</sup>Mo isotopes, which are unresolved due to their very close gyromagnetic ratios. A small peak at 63 MHz, which is resolved in the Ba<sub>2</sub>FeMoO<sub>6</sub> spectrum exhibits much different spin-echo shape from that in any other part of the spectrum. This feature is attributed to a <sup>57</sup>Fe signal. The spectra of the A<sub>2</sub>FeMoO<sub>6</sub> compounds include a main line at 55–68 MHz and a low frequency satellite at 40–50 MHz. They are attributed to ideal Mo sites and defect sites, i.e. antisite atoms and atoms in antiphase boundaries. The hyperfine field corresponding to the main line amounts to 19, 24 and 23 T for Ba, Sr and Ca compounds, respectively. From the hyperfine fields, the values of the Mo magnetic moment at ideal sites for Ba, Sr and Ca compounds were  $-0.48$ ,  $-0.60$  and  $-0.58 \mu_B$ , respectively. These values were obtained in the same way as in [3] and the hyperfine coupling constant used for this conversion was  $-40 \text{ T}/\mu_B$  [5].

The NMR spectra of the A<sub>2</sub>FeReO<sub>6</sub> compounds, Fig. 2, consist of signals of <sup>185</sup>Re and <sup>187</sup>Re isotopes, which are unresolved due to very similar values of their gyromagnetic ratios. Features of the resonant lines are due to a poor correction of the frequency response of the spectrometer. The values of the hyperfine fields derived from the resonance frequencies amount to 84, 94 and 95 T for Ba, Sr and Ca compounds, respectively. The hyperfine coupling constant of  $-100 \text{ T}/\mu_B$  was used [5]. The values of Re magnetic moments derived from

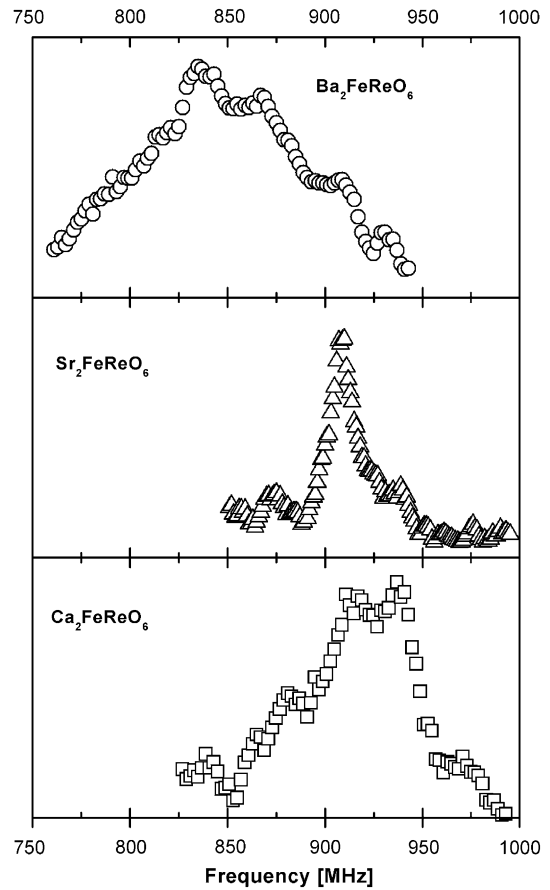


Fig. 2. <sup>185</sup>Re and <sup>187</sup>Re NMR spectra of A<sub>2</sub>FeReO<sub>6</sub> compounds at 4.2 K and zero external magnetic field.

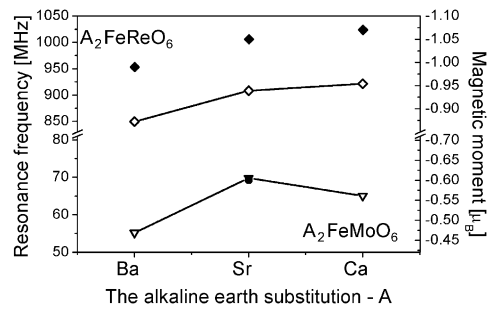


Fig. 3. Resonance frequencies (left axis) and magnetic moments at M=Mo or M=Re (right axis) of A<sub>2</sub>FeMO<sub>6</sub> for different alkaline earth compounds. Open triangles and rhombuses represent data obtained in this work. Filled circle and rhombuses correspond to theoretical values of magnetic moments from Ref. [6].

hyperfine fields amount to  $-0.87$ ,  $-0.94$  and  $-0.95 \mu_B$  for the Ba, Sr and Ca compounds, respectively. In analogy with the Mo moments they are assumed to be antiparallel to the Fe moments.

A plot of the main resonant frequencies and the corresponding values of magnetic moments are shown in Fig. 3, together with theoretical values of the magnetic moments obtained from Ref. [6]. For the case of the Mo compounds, there is very good agreement between the experimental and theoretical results. However, the experimental data for Re compounds are slightly lower than theoretically predicted, possibly due to an approximate value of the hyperfine coupling constant.

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