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Magnetic ordering in spin-chain $\text{Eu}_2\text{BaNiO}_5$ from ^{151}Eu Mössbauer measurements

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Abstract

We present ^{151}Eu Mössbauer measurements on $\text{Eu}_2\text{BaNiO}_5$, where the Ni^{2+} form well separated $S = 1$ antiferromagnetic chains. The appearance of magnetic moments in this compound evidences a 'crossed bootstrap' polarization since neither the Eu^{3+} nor the Ni^{2+} will carry magnetic moments unless polarized by an exchange field coming from the other sublattice. We confirm that the Eu^{3+} ion carries a magnetic moment below 30 K implying that Ni^{2+} ordered moments also appear below this temperature. We measure the thermal dependence of the size of the Eu^{3+} moment and of the polarizing field produced by the Ni^{2+} . Both show distributions which we link to the role of defects in the nickel chains. The measurements also provide the thermal dependence of the relative size of the Ni^{2+} moments. We compare the rare earth and nickel properties of $\text{Eu}_2\text{BaNiO}_5$ with those of isomorphous compounds.

1. Introduction

In Y_2BaNiO_5 , the Ni^{2+} ions form an arrangement of well separated linear chains aligned along the a -axis [1, 2]. The Ni^{2+} ion has an $S = 1$ ground state and the relatively strong intra-chain interaction leaves a ground state which is a non-magnetic singlet and a gap of approximately 120 K to the lowest excited state [3, 4]. The Ni^{2+} thus behave according to the Haldane scenario for uncoupled antiferromagnetic Heisenberg $S = 1$ chains. The Y^{3+} may be replaced by most of the magnetic rare earths (R^{3+}) without affecting the crystal structure [2, 5]. The presence of magnetic rare earth ions introduces a coupling between the chains such that ordered magnetic moments appear in both the Ni^{2+} and the R^{3+} sublattices [5–8] at a common long range magnetic ordering temperature. The magnetic polarization of the Ni^{2+} does not lead to the suppression of the gap, which is rather renormalized in the magnetically ordered region [9].

For the different $R_2\text{BaNiO}_5$, the magnetic properties of the Ni^{2+} and the R^{3+} as well as the various interactions between them, are found to depend on the particular rare earth [5–15]. The compounds with $R^{3+} = \text{Nd}^{3+}$, Gd^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+} have all been considered within the same self-consistent empirical model where the induced Ni^{2+} moment is expressed as a monotonic, non-linear function of the ordered moment appearing within the rare earth sublattice [13, 14, 16]. It seems likely that the thermal dependence of the moments for $R^{3+} = \text{Tm}^{3+}$ [5, 17] can also be well interpreted with this model.

Amongst the rare earths, the Eu^{3+} ion is particular in that its electronic ground state is a spin–orbit derived singlet ($J = 0$), which has no intrinsic magnetic moment. It may only acquire a moment through being mixed with the first excited state ($J = 1$) by an applied or exchange field. A plausible initial scenario for $\text{Eu}_2\text{BaNiO}_5$ would be that since the Eu^{3+} ion does not carry an intrinsic magnetic moment, then the Ni^{2+} will not be polarized and it will also not carry any magnetic moment. In such a case the compound would remain devoid of ordered magnetic moments and it would behave in an analogous manner to Y_2BaNiO_5 . However, an optical spectroscopy study of $\text{Eu}_2\text{BaNiO}_5$ has shown that Eu^{3+} magnetic ordering does occur near 25 K [18] implying that Ni^{2+} magnetic ordering also occurs at the same temperature. This is an intriguing result, not only because it indicates that the magnetic coupling between the two singlet state sublattices is strong enough to introduce magnetic moments, but also because the reported magnetic ordering temperature is anomalously high when compared to the evolution observed for the other $R_2\text{BaNiO}_5$ (see below).

Apart from the quoted optical study, no other information appears to be available concerning $\text{Eu}_2\text{BaNiO}_5$. Due to the high Eu neutron cross-section, it is difficult to carry out a neutron diffraction study of Eu^{3+} or Ni^{2+} magnetic ordering in this compound. We present a ^{151}Eu Mössbauer absorption study of polycrystalline $\text{Eu}_2\text{BaNiO}_5$ which confirms the existence of Eu^{3+} magnetic ordering and provides new information concerning the thermal dependence of the absolute sizes of the Eu^{3+} moments and the relative sizes of the Ni^{2+} moments as well as concerning the exchange couplings between the two sublattices.

We first recall the relevant 4f shell and hyperfine properties of the Eu^{3+} ion and, in turn, we present the ^{151}Eu Mössbauer analysis and then discuss the information obtained concerning the induced Eu^{3+} and Ni^{2+} moments and the coupling between the two sublattices.

2. The hyperfine field and magnetic moment of the Eu^{3+} ion

The Eu^{3+} ion has six electrons in the 4f shell, and the spin–orbit derived ground state is a singlet, 7F_0 . In absence of a molecular or an applied magnetic field it carries no magnetic moment. When a field is present, a 4f shell magnetic moment is induced through quantum mixing with the excited spin–orbit levels (7F_1 , 7F_2 etc) which lie near 500, 1300 K etc. The relation between the size of the induced magnetic moment and that of the inducing molecular field was initially described by second-order perturbation theory involving the lowest excited spin–orbit level [19]. A second-order treatment involving the two lowest excited spin–orbit levels was also used to provide the Eu^{3+} hyperfine field [20]. Relations were also obtained between the magnetic moment, the hyperfine field and the molecular field following complete diagonalization within the levels of 7F_1 , 7F_2 and 7F_3 [21].

The comparison of these calculations shows that the second-order treatment involving only the lowest excited spin–orbit level provides a satisfactory description at low temperatures provided that the three related parameters (magnetic moment, exchange field and hyperfine field) remain small. These conditions are indeed satisfied in $\text{Eu}_2\text{BaNiO}_5$. Using the second-order treatment, the relations linking the induced Eu^{3+} magnetic moment (M^{Eu}) and the induced

Eu hyperfine field ($H_{\text{hyp}}^{\text{Eu}}$) with the exchange field ($H_{\text{ex}}^{\text{Eu}}$) are linear and can be written as

$$M^{\text{Eu}} = 16 \frac{\beta^2 H_{\text{ex}}^{\text{Eu}}}{\Delta E} \quad (1)$$

$$H_{\text{hyp}}^{\text{Eu}} = \frac{80}{3} \frac{\beta^2 \langle r^{-3} \rangle H_{\text{ex}}^{\text{Eu}}}{\Delta E}, \quad (2)$$

where β is the Bohr magneton, ΔE is the separation between the F_0 and F_1 levels (~ 500 K) and $\langle r^{-3} \rangle = 5.7 \times 10^{25} \text{ cm}^{-3}$ [22].

As we find (see below) that the hyperfine field only exists below 30 K, that is, it exists at temperatures which remain small compared to $\Delta E/K$, then in $\text{Eu}_2\text{BaNiO}_5$, equations (1) and (2) remain valid at all temperatures where the hyperfine field exists.

Measurement of the thermal dependence of the ^{151}Eu hyperfine field thus provides the thermal variations of the Eu^{3+} magnetic moment and the exchange field acting on the Eu^{3+} ion. Considering that this field is produced by the magnetic moments of the Ni^{2+} of the chains (there is no evidence of any contribution to this field coming from within the rare earth sublattice), we write

$$H_{\text{ex}}^{\text{Eu}} = \alpha M^{\text{Ni}}. \quad (3)$$

where the coupling constant parameter α has the same definition as previously [14]. Its value cannot be obtained in the present case because the sizes of the Ni^{2+} moments are unknown.

Since there are twice as many Eu^{3+} as Ni^{2+} , the effective field acting on a Ni^{2+} ion due to the effective coupling with the Eu^{3+} sublattice is given by

$$H^{\text{Ni}} = 2\alpha M^{\text{Eu}} \quad (4)$$

and, using equation (1),

$$H^{\text{Ni}} = \frac{32\beta^2}{\Delta E} \alpha H_{\text{ex}}^{\text{Eu}}. \quad (5)$$

Equations (1), (3)–(5) thus provide links between the moments of (and the fields acting on) one sublattice and the moments of (and the fields acting on) the other sublattice.

In the next section we present the ^{151}Eu Mössbauer measurements of the hyperfine field and we obtain information concerning the various ionic magnetic parameters that are related to it. In section 4 we compare the values obtained with those for the other R_2BaNiO_5 .

3. Sample and ^{151}Eu Mössbauer measurements

The sample was made by heating the constituent oxides in air to 1100°C . Room temperature x-ray measurements showed that the structure type ($\text{Nd}_2\text{BaNiO}_5$; space group: $Immm$) is the same as for other R_2BaNiO_5 and the presence of some oxide impurities. The basic features of the crystal structure are shown in figure 1 of [14].

The ^{151}Eu Mössbauer absorption measurements were made over the temperature range 77–1.4 K using a source of Sm^*F_3 and a triangular velocity sweep. For ^{151}Eu , $I_g = 5/2$, $I_{\text{ex}} = 7/2$, $E_\gamma = 21.5 \text{ keV}$, $1 \text{ mm s}^{-1} = 17.4 \text{ MHz}$. Results at some selected temperatures are shown in figure 1. The isomer shift value ($\sim 1.1 \text{ mm s}^{-1}$) identifies the 3+ charge state.

At 77 K (figure 1) the absorption pattern takes the form of a single narrow line and the line fit evidences a small quadrupole interaction ($e^2q_{zz}Q/4 \simeq 0.14 \text{ mm s}^{-1}$ with η , the asymmetry parameter, ~ 1.0). This lineshape is independent of temperature down to 30 K, below which temperature the absorption pattern is influenced by the magnetic hyperfine interaction. The onset temperature for the magnetic hyperfine interaction is relatively well defined (figure 2):

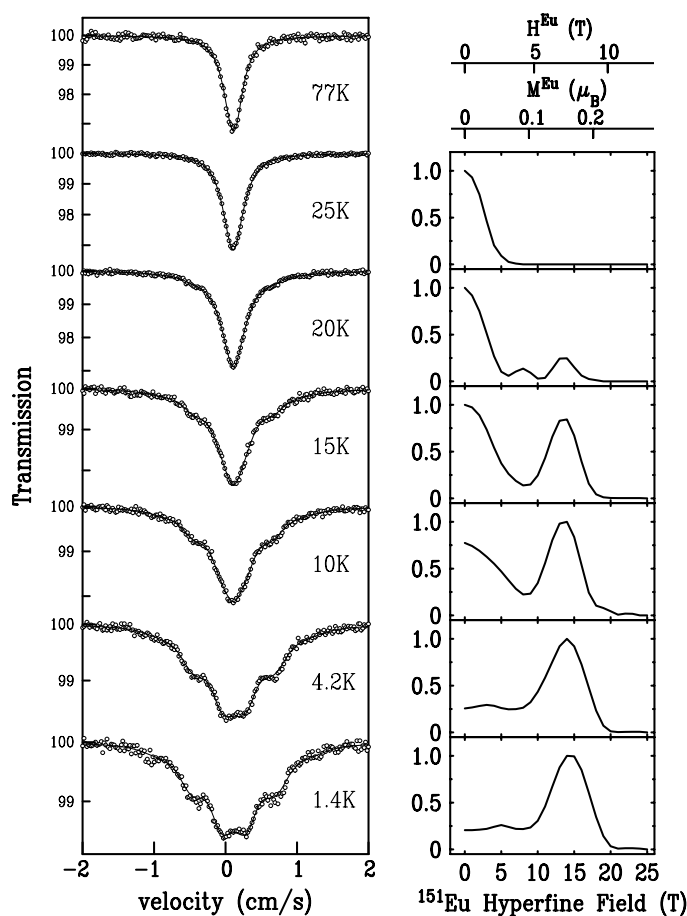


Figure 1. ^{151}Eu Mössbauer absorption spectra of $\text{Eu}_2\text{BaNiO}_5$ (left panel). A hyperfine field appears below ~ 30 K and the hyperfine field distributions are shown in the right panel. The exchange field acting on the Eu^{3+} (H^{Eu}) and the Eu^{3+} magnetic moment (M^{Eu}) are linearly related to the hyperfine field and their appropriate scales are also given.

the overall width of the absorption at 30 K is the same as that at 77 K and it increases by 10% when the temperature is further lowered to 25 K.

The measurement of the magnetic hyperfine field at low temperatures is facilitated by the fact that in its absence, the absorption takes the form of a single relatively narrow line. At low temperatures, we find that the spectra are not well fitted in terms of a unique hyperfine field and that satisfactory line fits may only be obtained by introducing hyperfine fields showing distributions. These distributions were obtained by fitting the data in terms of a histogram with 25 distinct hyperfine fields with values extending from 0 to 25 T using a standard χ^2 minimization procedure. The line intensities of each subspectrum were proportional to the appropriate Clebsch–Gordan coefficients [23]. The relative weights associated with each of the hyperfine fields were then treated as adjustable. The smoothed forms of the histograms of the hyperfine field distribution are given on the right-hand side of figure 1. Following equations (1) and (2), the hyperfine field distributions can also be expressed as distributions in the size of the Eu^{3+} 4f shell magnetic moment and in the size of the exchange field acting on the Eu^{3+} and the corresponding scales are given above the histograms.

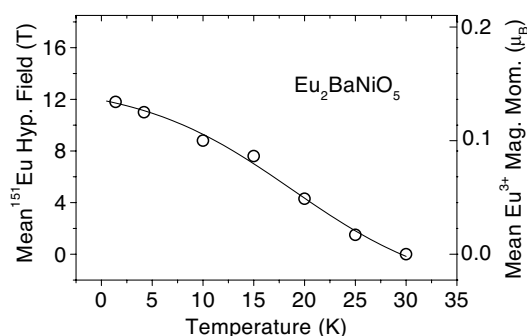


Figure 2. From ^{151}Eu Mössbauer absorption measurements on $\text{Eu}_2\text{BaNiO}_5$, the thermal dependence of the average hyperfine field and of the average Eu^{3+} magnetic moment obtained from the distributions shown in figure 1. The line is a guide to the eye.

The hyperfine field distributions show that the fields which initially appear as the temperature is lowered below 30 K have small values (<5 T). At lower temperatures the fields extend to an upper limit of ~ 20 T. At 20 K, the hyperfine field distribution evidences a small peak which is centred at 14 T. As the temperature is lowered, the peak remains at essentially the same field strength and its intensity increases and then saturates. The distributions thus evidence two well defined features: a low field tail which dominates at high temperatures and a broadened peak, at 14 T, which dominates at low temperatures. The minor peaks which appear in the distributions at some temperatures are not well established since their intensities fall within the error bars of the analysis.

We note that the Eu^{3+} moments are of the order of a fraction of a μ_B and the exchange fields that they experience extend up to ~ 10 T. The peak in the distribution of the exchange field acting on the Eu^{3+} moment occurs at 7.4 T and that in the Eu^{3+} magnetic moment at $0.17 \mu_B$.

The thermal dependence of the average value of the Eu^{3+} hyperfine field (and of the Eu^{3+} magnetic moment) is shown in figure 2. The thermal variation has a similar form to that of the average Eu^{3+} magnetic splitting measured optically [18]. However, this presentation of an average value obscures the true behaviour of the magnetic polarization which rather involves the distributions of figure 1.

4. Discussion

The limiting low temperature (1.4 K) magnetic moment distribution (figure 1) comprises a broadened peak with a relative weight corresponding to $\sim 80\%$ of the Eu^{3+} (and to the exchange fields coming from the Ni^{2+}) and a low side tail corresponding to the remainder. We suggest that the broad nature of the peak and the existence of a tail are both linked to the presence of defects within the Ni^{2+} chains. These defects are essentially paramagnetic Ni^{2+} , which break the chains into segments. The defects are most directly evidenced in Y_2BaNiO_5 by a low temperature upturn in the magnetic susceptibility [3]. Our sample of $\text{Eu}_2\text{BaNiO}_5$ also evidences similar behaviour. In $\text{Eu}_2\text{BaNiO}_5$, as in the isomorphous compounds, we anticipate that the segments remain long enough that there are more Ni within the segments than at their extremities. We thus suggest that the dominant peak in the distribution is due to the Eu^{3+} linked with the Ni^{2+} which lie within the segments and that the tail corresponds to the Eu^{3+} which are influenced more strongly by the Ni between and/or at the ends of the chains. The Mössbauer evidence (microscopic probe) showing that there is a significant distribution in the properties of the rare earth in $\text{Eu}_2\text{BaNiO}_5$ contrasts with the results of analogous Mössbauer measurements

Table 1. Results for $\text{Eu}_2\text{BaNiO}_5$ together with those for six isomorphous R_2BaNiO_5 . T_M is the magnetic ordering temperature of the R^{3+} and Ni^{2+} sublattices with M^R and M^{Ni} their saturated magnetic moments (the value of M^{Ni} for $\text{Gd}_2\text{BaNiO}_5$ was obtained indirectly). H_M^R and H_{ex}^R are respectively the saturated molecular and exchange fields acting on the rare earth sublattice with the link between the two given in the text. H^{Ni} is the saturated molecular field on the Ni^{2+} sublattice. For Eu^{3+} , where M^R and H^R evidence distributions, the values correspond to the peaks in the distributions which are $\sim 15\%$ higher than the average values. E_{ex}^R is the rare earth exchange energy defined in the text.

| | T_M (K) | M^R (μ_B) | H_M^R (T) | H_{ex}^R (T) | E_{ex}^R (K) | M^{Ni} (μ_B) | H^{Ni} (T) | Reference |
|------------------|-----------|-------------------|-------------|-----------------------|-----------------------|-----------------------------|---------------------|-----------|
| Nd^{3+} | 48 | 2.68 | 12.7 | -17 | 22.9 | 1.55 | 43.9 | [13] |
| Gd^{3+} | 59 | 7.0 | 8.9 | 8.9 | 41.7 | (1.6) | 77.0 | [16, 26] |
| Dy^{3+} | 65 | 7.9 | 4.3 | 8.6 | 22.8 | 1.53 | 44.7 | [26] |
| Er^{3+} | 33 | 7.9 | 2.8 | 8.4 | 14.9 | 1.54 | 28.9 | [13, 26] |
| Tm^{3+} | 14.5 | 3.5 | 1.4 | 4.9 | 3.3 | — | — | [5, 17] |
| Yb^{3+} | 8.8 | 0.6 | 13.9 | 55.6 | 5.6 | 1.07 | 15.6 | [14] |
| Eu^{3+} | 30 | 0.17 | — | 7.4 | 1.7 | — | — | This work |

on other R_2BaNiO_5 [14, 16, 24, 25] which show little, if any, influence of distributions in the sizes of the rare earth magnetic moments.

We suggest that the evidence indicating the importance of distributions in $\text{Eu}_2\text{BaNiO}_5$ does not necessarily show that this compound has more defects within the chains. The distributions could also be linked to the fact that the rare earth moments are induced: for a Kramers ion, the limiting low temperature moment has the same value whatever the size of the molecular field that it experiences, whereas when the moments are induced, the limiting low temperature moment continues to depend on the size of the molecular field.

The values for the different parameters are given in table 1 which also presents the values for the equivalent parameters in the other R_2BaNiO_5 . For the rare earths where $J \neq 0$ in the ground state, the experiment provides the molecular field, H_M^R , acting on the rare earth and the rare earth exchange energy is given by

$$E_{\text{ex}}^R = M^R H_M^R. \quad (6)$$

For these cases, the exchange field H_{ex}^R is related to the molecular field by the expression

$$H_{\text{ex}}^R = \frac{gJ}{2(g_J - 1)} H_M^R. \quad (7)$$

For Eu^{3+} , where $J = 0$, the only relevant field is the exchange field and the exchange energy is given by

$$E_{\text{ex}}^R = 2\beta H_{\text{ex}}^R \langle S_z \rangle, \quad (8)$$

where $\langle S_z \rangle$ is the mean value of S_z in the ground state. As discussed in [27], in the ground state $\langle L_z + S_z \rangle = 0$ so the magnetic moment is

$$\langle M \rangle = \beta \langle S_z \rangle, \quad (9)$$

and the exchange energy is

$$E_{\text{ex}}^R = 2\langle M \rangle H_{\text{ex}}^R. \quad (10)$$

The result indicating that the magnetic ordering temperature for $\text{Eu}_2\text{BaNiO}_5$ is anomalously high in relation to its rare earth exchange energy is contained in the table and it is more clearly evidenced by the graphical presentation of figure 3. For the six other compounds, the ordering temperature differs by at most a factor of two from the linear dependence whereas for $\text{Eu}_2\text{BaNiO}_5$ it differs by almost an order of magnitude.

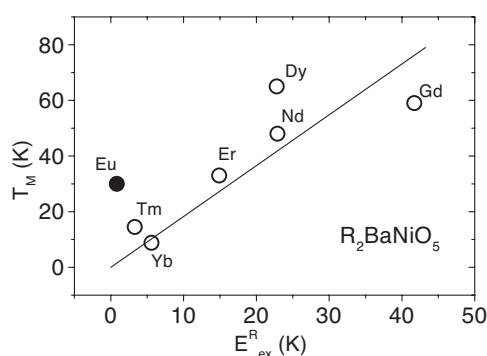


Figure 3. The magnetic ordering temperature, T_M , for different R_2BaNiO_5 as a function of the rare earth exchange energy, E_{ex}^{R} , which is defined in the text. The straight line fit to the data, excluding that for $\text{Eu}_2\text{BaNiO}_5$, indicates that in these cases, T_M increases approximately linearly with E_{ex}^{R} . The ordering temperature for $\text{Eu}_2\text{BaNiO}_5$ is much higher than that expected from the linear dependence.

In all the R_2BaNiO_5 , the rare earth–rare earth interaction plays, at most, a minor role indicating that the rare earth exchange energy is governed by the nickel–rare earth interaction. (The rare earth–rare earth interaction is however, not totally absent since it has been shown that if this were the case, three-dimensional magnetic order would not occur in the R_2BaNiO_5 in the presence of an isotropic Heisenberg interaction [15].) The anomalous high magnetic ordering temperature for $\text{Eu}_2\text{BaNiO}_5$ suggests that in this case other interaction energies, for example that relating to the coupling between the induced Ni^{2+} moments, play a more important direct role in establishing the magnetic ordering temperature. It has also been observed [24] that the magnetic ordering temperature shows a relatively smooth variation as a function of the estimated spin component of the rare earth (that is, of the quantity $J(g_J - 1)$, where crystal field effects were neglected). The results for $\text{Eu}_2\text{BaNiO}_5$, when added to this type of presentation, again differ considerably from the general trend.

It will be of interest to examine the properties of $\text{Eu}_2\text{BaNiO}_5$ using neutron diffraction so as to directly obtain the average sizes of the Ni^{2+} moments and the size of the coupling constant α of equation (3).

Finally, we mention that we carried out some ^{151}Eu Mössbauer measurements on a sample where 10% of the Ni^{2+} was replaced by Zn^{2+} . The aim was to intentionally decrease the average length of the Ni^{2+} chains and to examine possible changes in the magnetic properties. As might be expected, we find that the substitution does broaden the low temperature distributions and it does decrease the ordering temperature (to ~ 20 K). Surprisingly however, the presence of the Zn^{2+} leads to an increase both in the average size of the Eu^{3+} magnetic moment (by $\sim 25\%$) and in the value at the peak of the magnetic moment distribution (also by $\sim 25\%$). The Zn^{2+} substitution thus leads to an increase in size of the molecular field produced by the Ni^{2+} on the Eu^{3+} and it thus corresponds to an increase in the average size of the Ni^{2+} moment. Although the substitution of Zn^{2+} into the chains of Y_2BaNiO_5 does not introduce any magnetic order [28], the substitution of Zn^{2+} in $\text{Eu}_2\text{BaNiO}_5$ leads to an increase in the size of the ordered Ni^{2+} moments.

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