Magnetic properties of $Pnma$-R_2BaZnO_5 oxides (R = Sm, Eu, Dy and Ho)

Magnetic properties of $Pnma$-R$_2$BaZnO$_5$ oxides (R = Sm, Eu, Dy and Ho)

G F Goya†‡, R C Mercader†, M T Causa§ and M Tovar§

† Departamento de Física, Universidad Nacional de La Plata, 1900 La Plata, Argentina
§ Instituto Balseiro and Centro Atómico Bariloche, 8400 Bariloche, Argentina

Abstract. In this work, we report DC susceptibility measurements in the range 1.8–300 K on $Pnma$-R$_2$BaZnO$_5$ oxides with R = Sm, Eu, Dy and Ho. Eu$_2$BaZnO$_5$ displays Van Vleck paramagnetism which corresponds to the singlet ground state $^7F_0$ of Eu^{+3} ions, with a spin–orbit coupling constant value of $\lambda = 365(2)$ cm^{-1}. Sm$_2$BaZnO$_5$ also behaves as a Van Vleck paramagnet, with the magnetic ground multiplet split under the crystal–field interaction. For this compound we found that the ground state corresponds to an effective spin state S $(\pm\frac{1}{2})$, with effective magnetic moment $\mu_{eff} = 0.32(1)\mu_B$, and Van Vleck constant $\alpha_1 = 9.2(2) \times 10^{-4}$. For R = Dy and Ho, the magnetic susceptibility obeys a Curie–Weiss law down to $T = 1.8$ K, with effective moments close to the free-ion values. The absence of magnetic ordering above 1.8 K, together with the Curie temperatures $\theta_{Dy} = -15.1(8)$ K and $\theta_{Ho} = -11.3(8)$ K of these compounds, indicate the existence of competing interactions that frustrate the magnetic ordering.

1. Introduction

Ternary oxides of general formula R$_2$BaMO$_5$ (R = Y or rare earth and M = 3d transition metal) crystallize in four different structural types, depending on the R and M elements involved [1]. Systematic studies of these structures [2–7] with nearly all R and M elements revealed that the crystal structure of the different compounds is strongly associated with the 3d transition metal, but is almost independent of the R ion involved.

These systems also display a diversity of magnetic structures, many of them of low dimensionality [1, 8, 9]. Magnetic properties of $Pnma$-R$_2$BaCuO$_5$ members with magnetic R atoms have been investigated [10–13] but there is not yet a satisfactory explanation for the observed behaviour. This is mainly due to the coexistence of competing interactions that require complex descriptions in terms of intra- and inter-sub-system (R–R, R–M and M–M) parameters. It is therefore desirable to investigate the R–R and M–M intra-sub-lattice interactions separately, which would also help to clarify the R–M coupling mechanisms.

In order to study the R–R interactions, the R$_2$BaZnO$_5$ compounds provide a suitable frame because diamagnetic Zn^{2+} ions do not disturb the magnetic properties of the R sub-lattices. Since these compounds are isomorphous to R$_2$BaCuO$_5$, similar R–R exchange interactions are expected for both systems. In this paper we report DC magnetization measurements on R$_2$BaZnO$_5$ with R = Eu, Sm, Dy and Ho in the range 1.8 K $\leqslant T \leqslant$ 300 K and discuss the interpretation of the experimental data in terms of current theoretical models.

‡ Present address: Instituto de Física, Universidade de São Paulo, Caixa Postal 66318, 05389-970 São Paulo, Brazil.

2. Experimental

Samples of R_2BaZnO_5 (R = Eu, Sm, Dy and Ho) were prepared by standard solid state reaction from R_2O_3 (99.999%), CO_3Ba (99.99%) and ZnO (99.999%) powders mixed in stoichiometric amounts. The homogenized mixture was first fired in air at 500 °C, then re-ground and re-heated three times at 900 °C for 24 h. Powder x-ray diffraction characterization was performed using Cu-Kα radiation. X-ray data were refined using Rietveld profile analysis [14]. The DC magnetic susceptibility was measured in a SQUID magnetometer, in the range 1.8–300 K, in applied fields $H = 10^{-3}$–1 T.

3. Results and discussion

X-ray data of all samples showed a single phase that was indexed with an orthorhombic unit cell, *Pnma* space group, in agreement with previous structural data [4]. Figure 1 shows the magnetic susceptibility data of Eu_2BaZnO_5. The shape of the curve is characteristic of a Van Vleck paramagnet [15], with a constant value for the lower temperature range and a decreasing value when $T \geqslant 100$ K. The ground state $^7F_0$ of Eu^{3+} is non-magnetic and the excited states ^7F_J are close enough to give energy differences comparable to kT at room temperature (≈ 205 cm^{-1}). When Russell–Saunders coupling is assumed, the energy levels W_J can be written as [15]

$$W_J = \frac{\lambda}{2}[J(J+1) - L(L+1) - S(S+1)] + A \tag{1}$$

where λ is the spin–orbit coupling constant and A is a constant independent of J. The susceptibility per mole of Eu^{3+} is then given by

$$\chi(Eu^{3+}) = \left(\frac{C}{T}\right) \frac{(24/\gamma) + (13.5 - (3/2\gamma))\,e^{-\gamma} + (67.5 - (5/2\gamma))\,e^{-3\gamma} + \cdots}{1 + 3\,e^{-\gamma} + 5\,e^{-3\gamma} + \cdots} \tag{2}$$

with $\mathbb{C} = [N_A\mu_B^2/(3k)]$, where N_A and μ_B are Avogadro's number and the Bohr magneton, respectively. The parameter $\gamma = \lambda/(kT)$ is the ratio between the multiplet width and the thermal energy. Subsequent terms give negligible contributions to $\chi(T)$ in this temperature range.

The best fit to the experimental data is shown in figure 1 with a continuous line and corresponds to $\lambda = 365(2)$ cm^{-1}. This value is close to that previously reported [16] for $EuAlO_3$ (370 cm^{-1}) and about 20% larger than the value found [17] in Eu_2CuO_4 single crystals (303 cm^{-1}). The differences between these estimations may be due to additional contributions to $\chi(T)$ from the magnetic Cu ions in Eu_2CuO_4. The obtained value of λ indicates that the excited states are close enough to the ground state to have a non-negligible population at room temperature, giving the observed Curie-like behaviour in the high-temperature region ($T \geqslant 100$ K). At low temperatures, only the non-magnetic ground state $J = 0$ of Eu^{3+} is populated and the susceptibility becomes temperature-independent. Structural studies on Eu_2BaZnO_5 have shown that Eu ions occupy two inequivalent sites in the structure [18], with distorted trigonal symmetry. However, our measurements on powder samples do not allow the observation of the crystal field anisotropies.

The molar magnetic susceptibility of Sm_2BaZnO_5 is displayed in figure 2. At low temperatures, only the magnetic $^6H_{5/2}$ ground multiplet is populated, which is split by the crystal field. The susceptibility per mol of Sm^{3+} ions is given by [15]

$$\chi(Sm^{3+}) = \frac{1}{8} \frac{(C_1/(T - \Theta)) + \alpha_1 + (C_2/(T - \Theta))\,e^{-\Delta/T_+} \cdots}{3 + 4\,e^{-\Delta/T_+} \cdots} \tag{3}$$

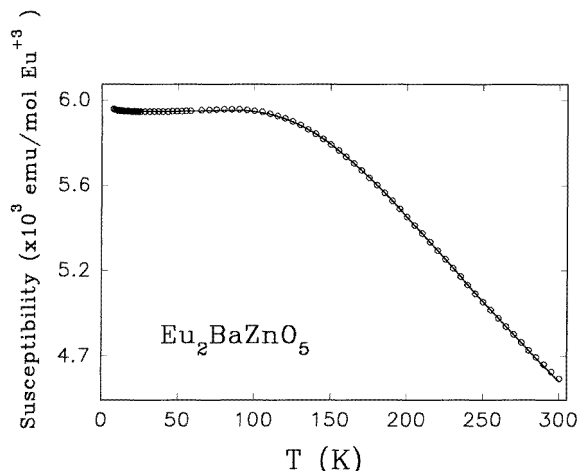**Figure 1.** Experimental (circles) magnetic susceptibility versus temperature for Eu$_2$BaZnO$_5$. The best fit to $\chi(T)$ (full line), using equation (2), was achieved for $\lambda = 365(2)$ cm^{-1}.

where Δ is the energy difference between the ground and first excited multiplet, and C_i and α_1 are the Curie and Van Vleck constants respectively. Δ and α_1 are not independent since $\alpha_1 = 1.07/\Delta$, if Δ is given in kelvins. Similarly to the Eu^{3+} case, for Sm^{3+} one also expects a non-negligible contribution from the excited state $^6\mathrm{H}_{7/2}$, which is $\Delta = 1100$ cm^{-1} above the $^6\mathrm{H}_{5/2}$ ground state [19]. In the 200 K $< T <$ 300 K region, the main contributions are given by

$$\chi(\mathrm{Sm}^{3+}) = \frac{C_1}{T} + \alpha_1 + \frac{C_2}{T}\,\mathrm{e}^{-\Delta/T} \tag{4}$$

with $C_2 = 7.44 \times 10^{-2}$. The fit to the experimental data (the full line in figure 2) gives $C_1 = 0.0545(1)$ emu K mol^{-1} and $\alpha_1 = 6.23(4) \times 10^{-4}$ emu mol^{-1} for the Curie and Van Vleck constants respectively. The corresponding value for the calculated effective moment is $\mu_{eff} = 0.66(2)\mu_B$.

The susceptibility in the low-temperature region (taken as $T \leqslant 10$ K) was fitted using the expression

$$\chi(\mathrm{Sm}^{3+}) = \frac{C_1'}{T - \Theta} + \alpha_1' \tag{5}$$

where we have introduced a Curie–Weiss behaviour to take into account the Sm–Sm exchange interactions. The best fit to the experimental data (see figure 2) corresponded to $\Theta = -1.0(1)$ K, $\alpha_1' = 9.2(2) \times 10^{-4}$ emu mol^{-1} and $C_1' = 0.0131(5)$ emu K mol^{-1}. These results indicate a strong reduction of the magnetic moment at low temperature ($\mu_{eff}' = 0.32(1)\mu_B$), probably due to crystal field splitting.

In the simplest case of an axial crystalline field, the ground state doublet may be either $S(= \pm\frac{1}{2})$ or $S(= \pm\frac{5}{2})$, with effective magnetic moments of $0.25\mu_B$ and $1.24\mu_B$ respectively. Our results from the low-temperature region indicate that the ground state is closer to $S = \pm\frac{1}{2}$. At higher temperatures the $^6\mathrm{H}_{7/2}$ excited state becomes accessible, contributing to the total measured susceptibility (the third term in equation (4)). At room temperature, the free-ion magnetic moment ($\mu_{eff}^{free} = 0.84\mu_B$) is not fully recovered.
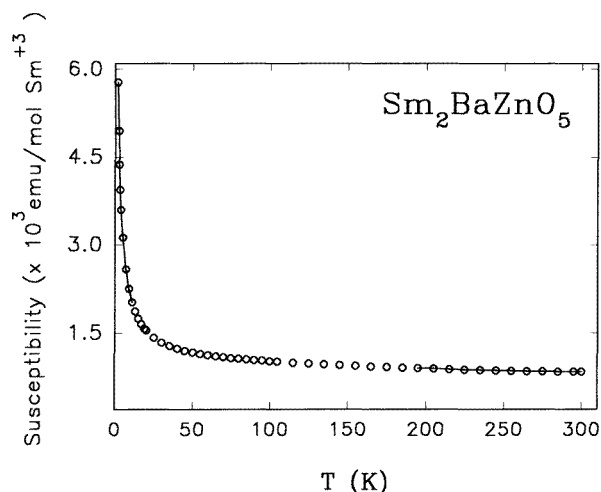
Figure 2. Magnetic susceptibility versus temperature data for Sm_2BaZnO_5. The high (equation (4)) and low (equation (5)) temperature fits to $\chi(T)$ are shown by full lines.

Previous specific heat and optical absorption measurements in Sm_2BaCuO_5 [11, 20] have shown two separate Néel temperatures at $T_{N1} = 22$ K and $T_{N2} = 5$ K, assigned to Cu and Sm ordering respectively. Our small value of Θ_{Sm} in Sm_2BaZnO_5, suggests that Sm ordering in Sm_2BaCuO_5 may be partially induced by the Cu sub-lattice.

Figure 3 shows the magnetic susceptibility data of Dy_2BaZnO_5 and Ho_2BaZnO_5 in the range 1.8 K $\leqslant T \leqslant$ 300 K at $H = 50$ mT. Both systems are paramagnetic down to 1.8 K, and were fitted with a Curie–Weiss law. The effective magnetic moments obtained for Dy^{3+} and Ho^{3+} in R_2BaZnO_5 (table 1) are similar to previous values found in $R_2Cu_2O_5$ [1, 21] and $RBa_2Cu_3O_7$ [22, 23]. These values are consistent with the expected ones within the L–S Russell–Saunders coupling scheme (labelled μ_{Hund} in table 1), assuming that $\Delta E \gg kT$ at room temperature, where ΔE is the energy difference between the excited and ground states of the electronic multiplet.

Table 1. Mean field parameters obtained from a Curie–Weiss fit of $\chi(T)$. μ_{exp}, experimental magnetic moments; Θ, Weiss temperature. Errors are quoted in parentheses. The calculated magnetic moments within Hund's approximation (μ_{Hund}) are shown for comparison. Data for Gd_2BaZnO_5 are from [24].

Compound	μ_{exp}	μ_{Hund}	Θ (K)
Gd_2BaZnO_5	7.99(1)	7.94	−15.9(3)
Dy_2BaZnO_5	10.84(2)	10.65	−15.1(8)
Ho_2BaZnO_5	10.34(2)	10.61	−11.3(8)

We have recently reported [24] magnetic susceptibility and electronic paramagnetic resonance (EPR) measurements on Gd_2BaZnO_5, which showed that the antiferromagnetic interactions present can produce long-range ordering of the Gd sub-lattice at $T_N(Gd_2BaZnO_5) = 2.3$ K. As discussed there, the ratio between the Néel and Curie–Weiss temperatures, $|\Theta_{Gd}|/T_N \approx 7$, indicates the existence of competing interactions that lead to
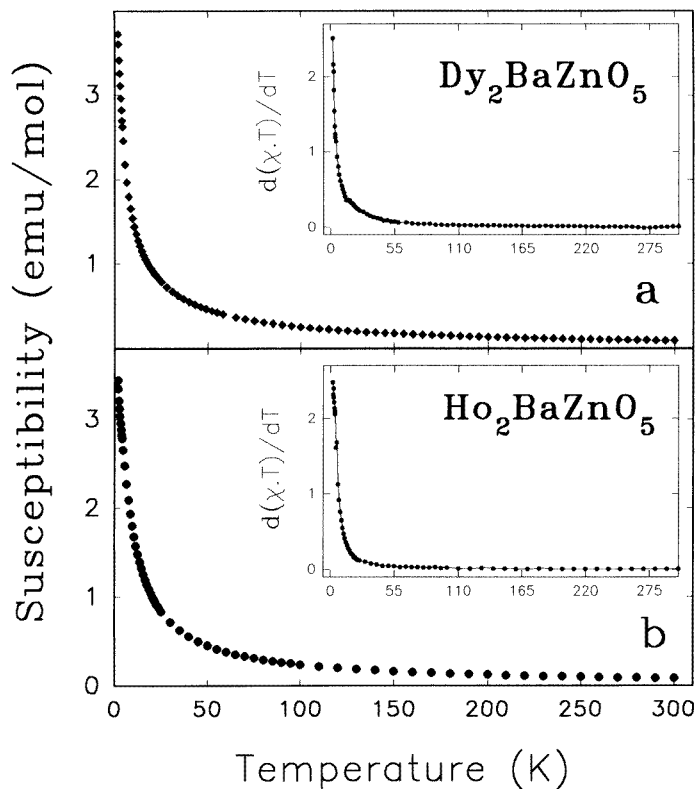
Figure 3. Magnetic susceptibility versus temperature data for Dy_2BaZnO_5 and Ho_2BaZnO_5. The insets show the $d(\chi T)/dT$ curves for each compound.

magnetic frustration in the system, originated in the multiplicity of R–R exchange pathways of this structure [24]. The coincident values found for the Curie–Weiss temperatures Θ_{Ho}, Θ_{Dy} and Θ_{Gd}, together with the common crystal structure of these compounds, suggest that similar exchange paths might be operative in all R_2BaZnO_5 samples.

It is interesting to note that the highest Néel temperature for the R sublattice (T_{N1}) in the R_2BaCuO_5 series is found [11] for R = Gd, with $T_{N1}(Gd_2BaCuO_5) = 12$ K. Correspondingly, the only transition above 1.8 K observed so far in the R_2BaZnO_5 family is for R = Gd $(T_N(Gd_2BaZnO_2) = 2.3$ K). The $d(\chi T)/dT$ curves for R = Dy and Ho (insets of figure 3), have very similar slopes and absolute values to those measured for Gd_2BaZnO_5 near T_N. This similarity suggests that the same R–R exchange interactions become operative, in the $T \lesssim 5$ K temperature range, for these systems. Thus it is plausible that the ordering temperature for Dy_2BaZnO_5 and Ho_2BaZnO_5 might be slightly below the lowest temperature of our experiment. Susceptibility measurements below $T = 1.8$ K would help to clarify this hypothesis.

In summary, we have measured the magnetic susceptibilities of several members of the R_2BaZnO_5 oxide system, in which the only magnetic ions are the rare earths. We have found Van Vleck magnetism and estimated the energy levels of the electronic multiplets for R = Eu and Sm in R_2BaZnO_5. For Sm^{3+} ions in Sm_2BaZnO_5, we have found evidence

that the ground state is $S = \pm\frac{1}{2}$. The compounds with R = Dy^{3+} and Ho^{3+} do not display magnetic ordering above 1.8 K. A mean field analysis leads to a relation of $\Theta/T_N > 5$ both for Dy_2BaZnO_5 and for Ho_2BaZnO_5, which indicates the existence of magnetic frustration in these systems, similar to previous findings in Gd_2BaZnO_5.

Acknowledgments

References

[1] Sáez-Puche R and Hernandez-Velasco J 1994 *Adv. Mater. Res.* **1** 65
[2] Michel C and Raveau B 1982 *J. Solid State Chem.* **39** 161
[3] Michel C and Raveau B 1982 *J. Solid State Chem.* **42** 176
[4] Michel C and Raveau B 1983 *J. Solid State Chem.* **49** 150
[5] Schiffler S and Müller-Buschbaum H K 1987 *J. Less Common Met.* **128** 117
[6] Buttner R H and Maslen E N 1993 *Acta Crystallogr.* B **49** 62
[7] Salinas-Sanchez A and Sáez-Puche R 1993 *Solid State Ionics* **63–65** 927
[8] Sachan V, Buttrey D J, Tranquada J M and Shirane G 1994 *Phys. Rev.* B **49** 14
[9] Batlogg B, Cheong S W and Rupp L W 1994 *Physica* B **194** 173
[10] Burriel R, Castro M, Piqué C, Salnas-Sánchez A and Sáez-Puche R 1992 *J. Magn. Magn. Mater.* **104–107** 627
[11] Levitin R Z, Mill B V, Moshchalkov V V, Samarin N A, Snegirev V V and Zoubkova J 1990 *J. Magn. Magn. Mater.* **90–91** 536
[12] Mehran F, Barnes S, Giess E A and McGuire T R 1988 *Solid State Commun.* **67** 55
[13] Golosovsky I V, Böni P and Fischer P 1993 *Solid State Commun.* **87** 1035
[14] Skthivel A and Young R A 1991 DBWS-9006PC, Program for Rietveld analysis of x-ray powder diffraction patterns, Georgia Institute of Technology, Atlanta
[15] Van Vleck J H 1965 *The Theory of Electric and Magnetic Susceptibilities* (London: Oxford University Press)
[16] Holmes L, Sherwood R and Van Uitert L G 1969 *Phys. Rev.* **178** 576
[17] Tovar M, Rao D, Barnett J, Oseroff S, Thompson J D, Cheong S-W, Fisk Z, Vier D C and Schultz S 1989 *Phys. Rev.* B **39** 2661
[18] Michel C and Raveau B 1982 *J. Solid State Chem.* **43** 73
[19] Arajs S 1960 *Phys. Rev.* **120** 756
[20] Paukov I V, Popova M N and Mill B V 1992 *Phys. Lett.* **169A** 301
[21] Seaman C L, Ayoub N Y, Bjørnholm T, Early E A, Ghamathy S, Lee B W, Markert J T, Neumeier J J, Tsai P K and Maple M B 1989 *Physica* C **159** 391
[22] Kazei Z A, Kolmakova N P, Levitin R Z, Mill B V, Moshchalkov V V, Orlov V N, Snegirev V V and Zoubkova Ja 1990 *J. Magn. Magn. Mater.* **86** 124
[23] Ganguly P, Sreedhart K, Raju A R, Damazeau G and Hagenmuller P 1989 *J. Phys.: Condens. Matter* **1** 213
[24] Goya G F, Mercader R C, Steren L B, Sánchez R, Tovar M and Causa M T 1996 *J. Phys.: Condens. Matter* **8** 4529