# A Study of Magnetic Interactions in $M_2EuRuO_6$ ($M$ = Ca, Sr, Ba) by $^{151}Eu$ Mössbauer Spectroscopy

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The series of compounds $M_2EuRuO_6$ ($M$ = Ca, Sr, Ba) has been studied by $^{151}Eu$ Mössbauer spectroscopy. X-Ray data show them to be structurally derived from the $ABO_3$ perovskite lattice, but only the Ba compound gives positive evidence to suggest ordering of the $Eu^{3+}/Ru^{5+}$ cations. The $^{151}Eu$ resonance shows magnetic hyperfine splitting at 4.2 K. The $Ru^{5+}$–O–$Eu^{3+}$–O–$Ru^{5+}$ exchange takes place by admixture of low-lying excited states into the diamagnetic $J = 0$ ground-state of the $Eu^{3+}$. The Curie temperatures are approximately 18, 31, and 42 K for the Ca, Sr, and Ba compounds. Detailed analysis shows that substantial disorder of cations occurs, being quite large for Ca, <8% for Sr, and <5% for Ba. However, it appears that considerable canting of the $Ru^{5+}$ spins takes place in the Ba compound immediately below the Curie temperature as a result of the disorder and low anisotropy at the Ru sites. This effect is much reduced in the more distorted Sr compound.

## Introduction

The magnetic properties of the recently prepared compounds of formula $M_2LnRuO_6$ ($M$ = Ca, Sr or Ba, $Ln$ = Y, rare earth, or Bi) are of particular interest (*1, 2*). Several of them crystallize with the ordered perovskite structure and contain the rare ruthenium (V) oxidation state; superexchange interactions between ruthenium ions can occur only through the path Ru–O–$Ln$–O–Ru, where $Ln$ is in some cases a diamagnetic cation. Similar superexchange interactions are believed to occur in another novel ruthenium (V) compound, $Na_3RuO_4$, which has been shown by $^{99}Ru$ Mössbauer spectroscopy to have long-range antiferromagnetic order despite the occurrence of isolated clusters of ruthenium cations (*3*).

In a recent paper (*2*) we described the $^{99}Ru$ Mössbauer spectra and X-ray powder diffraction data for a series of these perovskite phases including $Ca_2EuRuO_6$ and $Ba_2EuRuO_6$. The $^{99}Ru$ spectra at 4.2 K confirm the presence of magnetically ordered $Ru^{5+}$ cations, but throw little light on the order–disorder of the $Eu^{3+}/Ru^{5+}$ cations because the magnetic hyperfine field at the $Ru^{5+}$ is not very sensitive to changes in the local environment. In this work we have carried out a more detailed study of $M_2EuRuO_6$ ($M$ = Ca, Sr, Ba) using X-ray powder diffraction and the $^{151}Eu$ Mössbauer resonance. The latter has proved to be unusually sensitive to changes in the near-neighbor cations, and enables a detailed interpretation to be given.

## Crystallographic Data

Details of the preparation techniques and

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$^{99}$Ru spectra for $Ca_2EuRuO_6$ and $Sr_2EuRuO_6$ have already been given (2), but in view of the unusual $^{151}$Eu data obtained in the present work the X-ray characterization has been more closely investigated. Powder X-ray diffraction data were recorded with a Philips diffractometer using $CuK_\alpha$/Ni filtered radiation ($\lambda = 154.18$ pm). The slowest possible scanning speeds (1/8° per minute) were employed in order to obtain maximum resolution and accuracy.

### $Ca_2EuRuO_6$

Two separate preparations were made by heating to 1120°C for 4 (sample 1) and 31 days (sample 2), respectively. The diffraction pattern of the latter was indexed on the basis of a cubic perovskite cell of lattice parameter 795 ± 1.3 pm, together with several very weak reflections from an unidentified phase. The cubic phase appears to be similar to the compounds $La_2MRuO_6$ ($M$ = Mg, Mn, Ni, or Zn) reported by Galasso and Darby (4). While the cell edge is ca. 800 pm, the lattice nevertheless seems to be simple cubic and not face-centered cubic like the ordered perovskite compounds. Galasso comments (5) that the additional reflections are probably caused by a movement of ions from their positions in the ideal structure, and that for these compounds ordering of the $B$ cations has not been proved. Sample 1 gave a powder diffraction pattern very similar to that of sample 2, but several reflections were split, and could be indexed on the basis of a tetragonally distorted perovskite cell with $a = 796 \pm 1$ and $c = 787 \pm 1$ pm. The $^{151}$Eu Mössbauer spectra of samples 1 and 2 were indistinguishable.

### $Sr_2EuRuO_6$

Two samples were prepared by heating to 1150°C for 1 (sample 3) and 5 days (sample 4), respectively. The diffraction pattern of sample 4 closely resembled that of tetragonal $Ca_2EuRuO_6$ (sample 1), and

could be indexed with $a = 824.7 \pm 0.2$ and $c = 817.1 \pm 0.4$ pm. Again, the pseudocubic cell seems to be simple cubic and not face-centered cubic. Sample 3 gave a pattern almost identical to that of sample 4 except that the splittings were less resolved.

### $Ba_2EuRuO_6$

Two samples were prepared by heating to 1140°C for 1 (sample 5) and 3 days (sample 6), respectively. The powder diffraction patterns of both samples could be indexed on the basis of a face-centered cubic perovskite cell of the type where $B$ ions alternate at the corners of the simple unit cell (6). The lattice parameters were 840.5 ± 0.2 and 840.6 ± 0.1 pm, respectively. The superlattice reflections caused by ordering of the Eu and Ru cations (e.g., 111 and 311) were extremely weak, and were more diffuse in sample 5 than in sample 6. Thus in all three compounds there is evidence of a slow change upon prolonged annealing.

### Mössbauer Spectra

The $^{151}$Eu spectra of the six samples were obtained at various temperatures using established techniques (3, 7) and a source of $^{151}$Sm in $SmF_3$ at 4.2 K. Selected examples for $Ca_2EuRuO_6$ (sample 1), $Sr_2EuRuO_6$ (sample 3) and $Ba_2EuRuO_6$ (sample 6) are shown in Figs. 1–3. The $^{151}$Eu spectra show magnetic hyperfine splitting despite the formal ground state of $Eu^{3+}$ being a diamagnetic $J = 0$ state. As we shall show this is a result of the unusual exchange interaction between $Eu^{3+}$ and $Ru^{5+}$.

For comparison purposes the theoretical spectrum envelope for a single magnetic hyperfine field is given later in Fig. 5. It can be seen that the observed spectra are generally more intense in the central region at 4.2 K, a feature which becomes more enhanced with rise in temperature. At first sight this is not unlike the effects of relaxation; several
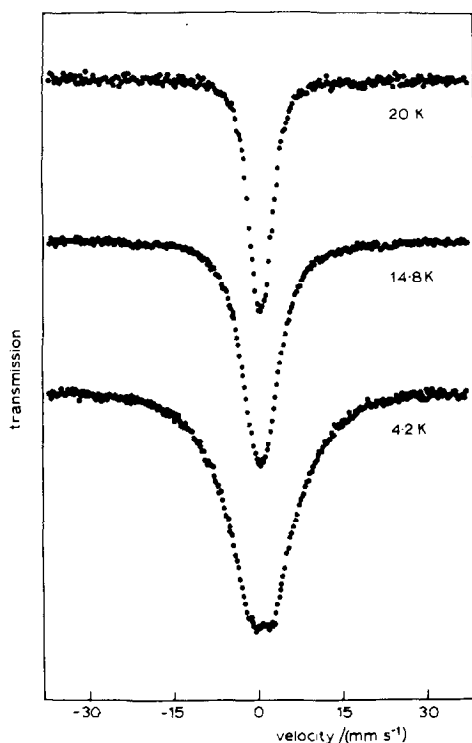
FIG. 1. The $^{151}$Eu spectra of Ca$_2$EuRuO$_6$ (sample 1) at 4.2, 14.8, and 20.0 K.

models for induced relaxation in $^{151}$Eu due to slow relaxation of the $^{99}$Ru spins were considered in detail. Although individual spectra could be reproduced on this basis, it quickly became clear that the predicted temperature dependence was quite different from that observed. We have therefore discarded this explanation, and do not discuss it further. However, a plausible explanation can be given in terms of an order–disorder model which encompasses both the X-ray and Mössbauer data.

## Exchange Interactions Involving Eu$^{3+}$ Ions

The exchange interaction between Ru$^{5+}$ and Eu$^{3+}$ is somewhat unusual. The ground state for Eu$^{3+}$ ($4f^6$) is $^7F_0$, which is diamagnetic. However, there are low-lying magnetic excited states, the $^7F_1$, state at approximately 538 K and the $^7F_2$ state at

1491 K ($8$). In the presence of an exchange interaction (in this case with Ru$^{5+}$) these excited states are mixed into the ground state which thereby produces a spontaneous magnetization and a nonzero magnetic hyperfine field at the Eu nucleus. Furthermore, thermal population of the excited levels can give a direct contribution which must also be considered. These ef-
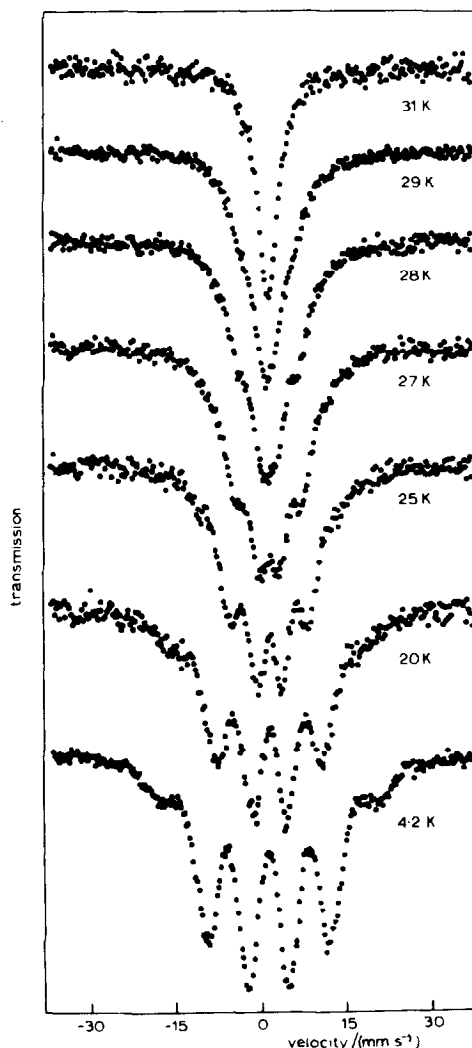


FIG. 2. The $^{151}$Eu spectrum of Sr$_2$EuRuO$_6$ (sample 3) as a function of temperature. Note the broad outer components and the more intense inner components. The absorption varies from 11% at 4.2 K to 25% at 31 K as the hyperfine pattern collapses.
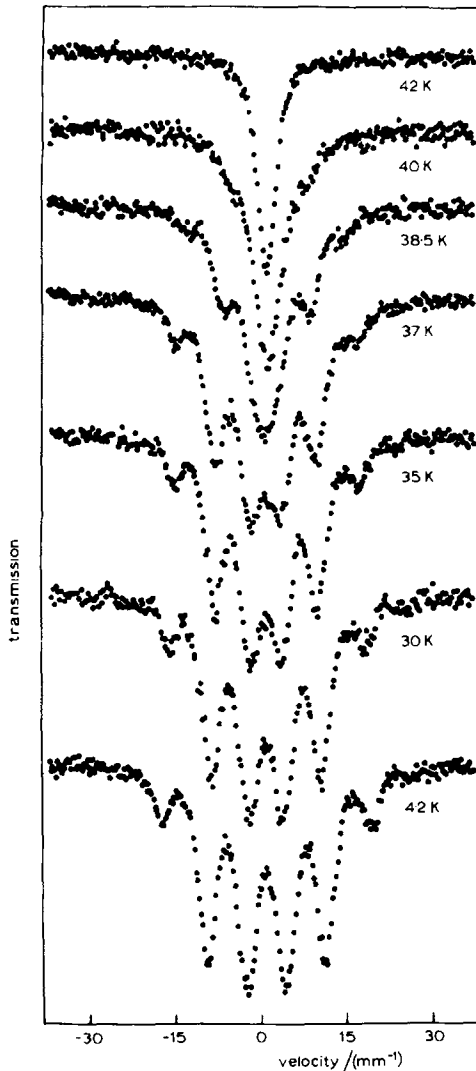
FIG. 3. The $^{151}Eu$ spectrum of $Ba_2EuRuO_6$ (sample 6) as a function of temperature. Note how the center of the spectrum increases in intensity at the expense of the wings. The absorption varies from 11% at 4.2 K to 25% at 40 K as the hyperfine pattern collapses.

fects have been fully investigated in europium iron garnet $Eu_3Fe_5O_{12}$ where exchange interaction with the $Fe^{3+}$ ions results in a hyperfine field at the $Eu^{3+}$ with a large magnetic flux density (63 and 57 T at 0 K at the two nonequivalent sites), together with a very unusual temperature depen-

dence of the field as a result of thermal population of the excited levels (8–11).

In the present work the energy-level scheme for $Eu^{3+}$ ($L = 3$, $S = 3$) has been calculated for the nine states $|L, S, J, J_z\rangle$ of $^7F_0 + {}^7F_1 + {}^7F_2$ using the Hamiltonian $H = E_J + 2\beta B_{ex}(T) \cdot S$, where $E_J$ is the energy of the unperturbed $^7F_J$ state, $\beta$ is the Bohr magneton, and $B_{ex}(T)$ is the flux density of the exchange field acting on the $Eu^{3+}$ ion at a temperature $T$. The matrix elements of the Hamiltonian can be evaluated and diagonalized to give the energy levels $E_i(T)$ and corresponding linear combinations of states $|i(T)\rangle$. The effective magnetic flux density at the europium nucleus corresponding to the state $i$ is given by $B_i(T) = \langle i(T)|B_z|i(T)\rangle$, where the operator $B_z$ is given by

$$B_z = 2\beta \left(\frac{\mu_0}{4\pi}\right) \langle r^{-3}\rangle \left\{\left(L_z - \frac{4}{45} S_z\right)\right.$$

$$\left. + \frac{1}{90} [(L \cdot S)L_z + L_z(L \cdot S)]\right].$$

The evaluation of $B_i(T)$ is complicated by this description in terms of both $L \cdot S$ and $J$, but is facilitated by the use of the relationships

$$|L, S, J, J_z\rangle = (-1)^{S-L-J_z}(2J + 1)^{1/2}$$

$$\sum_{L_z S_z} \begin{pmatrix} L & S & J \\ L_z & S_z & -J_z \end{pmatrix} |L, L_z, S, S_z\rangle,$$

where the expression in brackets is a 3-$j$ coefficient. The thermal population of the nine levels to give the observed effective magnetic hyperfine flux density $B_{eff}(T)$ is then obtained as

$$B_{eff}(T) = \sum_{i=1}^{9} B_i(T)\exp[-E_i(T)/kT]/$$

$$\sum_{i=1}^{9} \exp[-E_i(T)/kT].$$

This calculation has been performed by digital computer. The expectation value $\langle r^{-3}\rangle$ for $Eu^{3+}$ has been taken to be $49 \times 10^{-30}$ $m^{-3}$ (8). Crystal field effects are ex-

cluded from the calculation on the grounds that these are in any case small, particularly when the site symmetry is nearly cubic.

The Curie temperatures of the compounds described in the present work are below 50 K, so that thermal population of the $^7F_1$ states is quite small. The value of the observed flux density $B_{eff}(T)$ is consequently an almost linear function of the exchange field $B_{ex}(T)$, and does not show the more complex behavior found in the garnets. The precise temperature dependence of $B_{ex}(T)$ is unknown, but it is reasonable to assume that it follows the magnetization of the $Ru^{5+}$ cation, and will thus approximate to the $S = \frac{3}{2}$ Brillouin function.

The magnitude and temperature dependence of $B_{eff}(T)$ can now be expressed quite adequately in terms of the ordering temperature, $T_c$, and the limiting value of the flux density of the exchange field, $B_{ex}(0)$.

### Disorder Model for $M_2$EuRuO$_6$

All three compounds are structurally derived from the simple perovskite lattice, $ABO_3$, with both the $Eu^{3+}$ and $Ru^{5+}$ on the $B$ sites. The X-ray data for $Ca_2$EuRuO$_6$ and $Sr_2$EuRuO$_6$ would suggest that these cations may not be ordered. On the other hand, as we shall now show, the $^{151}$Eu magnetic hyperfine pattern at 4.2 K in $Sr_2$EuRuO$_6$ is only compatible with a substantial but incomplete ordering of the cations. The same is true for $Ba_2$EuRuO$_6$ despite the X-ray evidence for ordered cations on the $B$ sites. However, $Ca_2$EuRuO$_6$ appears to retain a high degree of disorder.

The hyperfine field at the $Eu^{3+}$ ion will be very sensitive to changes in its immediate environment because it is an induced rather than an intrinsic field; far more so in fact that the hyperfine field at $Ru^{5+}$ which derives entirely from the intrinsic $S = \frac{3}{2}$ state of the ion. Measurements of the $^{99}$Ru resonance in $Ca_2$EuRuO$_6$ and $Ba_2$EuRuO$_6$ at 4.2
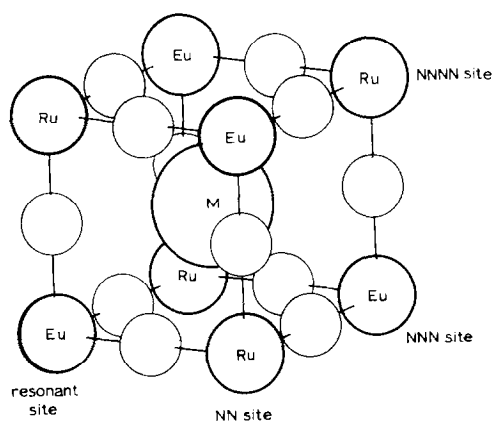


FIG. 4. The ordered perovskite lattice of $M_2$EuRuO$_6$.

K confirmed the presence of magnetically ordered $Ru^{5+}$ cations, but did not reveal any major differences between the two compounds (2).

Let us assume that the actual structure is closely related to the cubic perovskite structure by an alternation of the $B$-site cations as shown in Fig. 4 (only half the lattice dimensions of the unit cell are shown). Ordered perovskites of the type $M_2M'M''O_6$, where $M'$ is diamagnetic usually become antiferromagnetic by ordering of the second type in which interaction is between next-nearest $M''$ neighbors via the exchange route $M''-O-M'-O-M''$. For example, neutron diffraction data for $Ba_2$NiWO$_6$ show that ferromagnetic (111) layers of moments are coupled antiparallel to adjacent layers by this mechanism (12). If $M'$ is paramagnetic then the magnetic structure is often of $G$ type with antiparallel coupling of the $M''$ and $M'$ lattices via the exchange route $M''-O-M'$ to give a ferrimagnetic moment. This type has been positively characterized in $Sr_2$FeMoO$_6$ (13). Although the $Eu^{3+}$ has a diamagnetic $J = 0$ ground state, a magnetic moment is induced by the exchange coupling. The presence of a large hyperfine flux density at the $Eu^{3+}$ ion would suggest that the compound is ferrimagnetic with parallel alignment of

the $Ru^{5+}$ moments. The magnetic susceptibility data for $Ba_2EuRuO_6$ from 80 to 300 K show an unusually large negative value for the paramagnetic Curie temperature of $-1000$ K which is not inconsistent with ferrimagnetic order.

If the lattice were fully ordered then all $Eu^{3+}$ atoms would be interacting with six nearest-neighbor (NN) $Ru^{5+}$ atoms and would be equivalent; however, the $^{151}Eu$ spectra do not show a simple hyperfine pattern with a single value of the magnetic flux density and are inconsistent with this simple model.

If, on the other hand, there is a degree of disorder such that a fraction $c$ of the ions are randomly placed on the wrong sites, then the induced field at the $Eu^{3+}$ ions will be substantially modified. The probability $P(n)$ that $n$ of the NN sites are occupied by $Ru^{5+}$ will be given by the binomial distribution $P(n) = [6!/n!(6 - n)!](1 - c)^n c^{6-n}$.

If it is assumed that all n $Ru^{5+}$ spins lie parallel, then the exchange field at the $Eu^{3+}$ ion at the normal resonant site, $B_{ex}(T)$, will be proportional to $n$. The observed flux density $B_{eff}(T)$ is an almost linear function of $B_{ex}(T)$, so that to a good approximation $B_{eff}(T)$ is also proportional to $n$.

In addition to the NN site interaction, there may also be a minor contribution from $Ru^{5+}$ ions substituting on the 12 next-nearest-neighbour (NNN) sites, and a contribution from the 8 next-next-nearest-neighbour (NNNN) sites via the linear path $Eu^{3+}-M^{2+}-Ru^{5+}$. However, these will be much smaller than the NN interaction, and detailed computer calculations showed that when $c$ is small the effects of NN and NNNN substitution are so similar as to be indistinguishable. The NNNN interactions have therefore not been considered separately in the final analysis, although their contribution is effectively included.

A much more important contribution to the spectrum comes from the fraction $c$ of the $Eu^{3+}$ ions occupying $Ru^{5+}$ sites. If $c$ is

small the 6 NN sites are nearly all $Eu^{3+}$ ions, and it seems likely that the $Eu^{3+}-O-Eu^{3+}-O-Ru^{5+}$ exchange will be weak. However, the 12 NNN sites are now mainly occupied by $Ru^{5+}$, and could conceivably produce a significant exchange field.

A computer program was written to calculate theoretical hyperfine patterns for a fractional disorder $c$ and with varying exchange fields from NN and NNN sites under the assumption that all the $Ru^{5+}$ spins lie parallel to each other. The $Ru^{5+}$ spins on $Eu^{3+}$ sites are likely to couple antiferromagnetically via the $Ru^{5+}-O-Ru^{5+}$ exchange, but the possibility of ferromagnetic coupling was also considered. The effective exchange field was taken to be a linear sum of the NN and NNN contributions in proportion to the site occupancy.

The $^{151}Eu$ magnetic hyperfine pattern is produced by $M1$ transitions from the $I_g = \frac{5}{2}$ ground state to the $I_e = \frac{7}{2}$ excited state, and has 18 component lines which overlap considerably. Because of a large hyperfine anomaly in $^{151}Eu$, the ratio of magnetic moments appropriate to the analysis depends on the origins of the hyperfine field; as the present case is analogous to europium iron garnet the value of $\mu_e/\mu_g = 0.7465$ has been used ($14$), together with $\mu_g = +3.4649\ \mu_N \equiv 1.5206$ mm sec$^{-1}$ T$^{-1}$.

The computed spectrum shape using parameters appropriate to $Sr_2EuRuO_6$ at 4.2 K, $B_{eff}(4.2) = 28.0$ T for 6 NN $Ru^{5+}$ ions and a linewidth of $\Gamma = 2.2$ mm sec$^{-1}$, is shown in Fig. 5 as a function of the disorder parameter $c$. The contribution from $Eu^{3+}$ ions on $Ru^{5+}$ sites is also shown, and it is assumed that NNN and NNNN contributions are zero. When $c = 0$ the spectrum corresponds to a single hyperfine pattern. As $c$ increases the inner components increase in intensity relative to the outer ones which also broaden considerably. For a disorder corresponding to $c = 5\%$ the $Eu^{3+}$ ions on the wrong sites make a significant central contribution to the spectrum, and
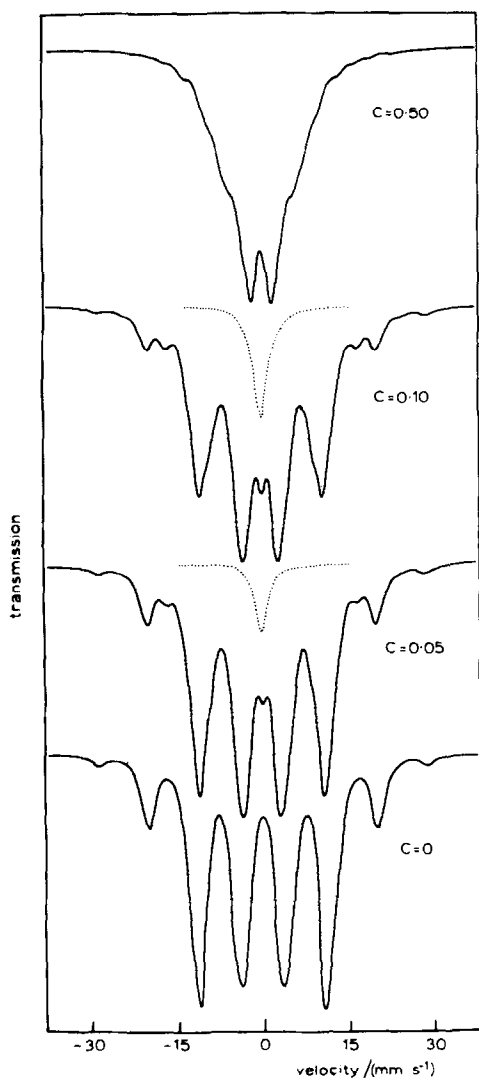
FIG. 5. The computed spectrum for $Sr_2EuRuO_6$ at 4.2 K as a function of the disorder parameter $c$. The contribution from $Eu^{3+}$ ions on $Ru^{5+}$ sites is shown as dotted lines.

this is even more marked at $c = 10\%$. However, this augmentation in the center of the spectrum can be largely removed by introducing a moderate exchange field from the 12 NNN sites. When $c$ increases to 50%, corresponding to complete disorder, the two components become equivalent and very substantial collapse of the spectrum has occurred; the overall result is not

dissimilar to the spectrum of $Ca_2EuRuO_6$ at 4.2 K.

By inspection of the spectra for $Sr_2EuRuO_6$ and $Ba_2EuRuO_6$ at 4.2 K it can be seen that these materials could have a disorder of about 8 and 5%, respectively. From the central region of the spectra it would appear that NNN effects are much greater in the Sr compound. Deviations from stoichiometry are not considered to be a significant factor in these samples. The weight loss on heating was small in all cases, and different preparations of the same nominal composition showed only minor differences. Saturation of the spectrum intensity would lead to effects in opposition to those created by disorder, and clearly does not explain the observed spectra.

The calculations we have carried out ignore all consequences of site distortion and spin canting. Both of these factors could lead to a spread in the effective values of the hyperfine field, thereby producing selective broadening of the outer lines of the spectrum and accentuating the effects of disorder. The figures of 8 and 5% can therefore be taken to be an upper limit; the true degree of disorder could be somewhat less.

Simulated spectra for $Sr_2EuRuO_6$ at 4.2, 20, 25, and 27 K are shown in Fig. 6. The degree of disorder is taken to be 8%, and the exchange field from 12 NNN sites is assumed to be 20% of that from 8 NN sites and of the same sign (i.e., ferromagnetic). As the spectrum collapses the changing cross section at any given Doppler velocity is compensated for by an increase in the effective linewidth parameter from 2.2 mm sec$^{-1}$ at 4.2 K to 3.0, 3.3, and 3.8 mm sec$^{-1}$ at the higher temperatures. The experimental linewidth at 31 K above the Curie temperature is 4.56 mm sec$^{-1}$. The agreement with experiment is reasonable, bearing in mind the many assumptions inherent in the model. Changing the sign for the exchange
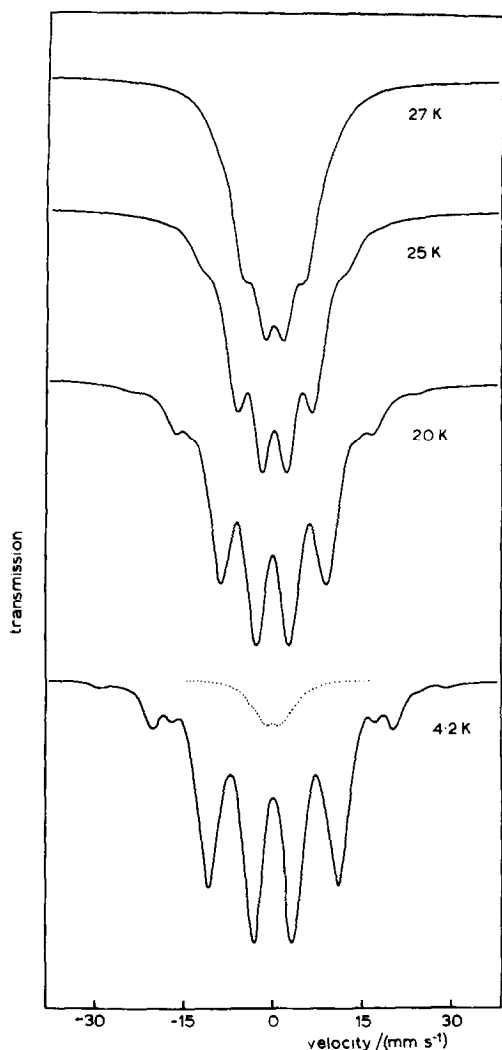
FIG. 6. Simulated spectra for $Sr_2EuRuO_6$ at 4.2, 20, 25, and 27 K using the order–disorder model described in the text.

field from NNN sites (i.e., antiferromagnetic coupling) produces only small changes, which are not considered significant.

The magnetic flux density for $Eu^{3+}$ ions in $Sr_2EuRuO_6$ with six NN sites occupied by $Ru^{5+}$ is shown in Fig. 7 as function of temperature. Also shown is a calculated curve assuming that the $Ru^{5+}$ exchange field follows the S = $\frac{3}{2}$ Brillouin function and using the full model for the $^7F_0$ +

$^7F_1$ + $^7F_2$ states of $Eu^{3+}$ with $B_{eff}(0)$ = 28.0 T and $T_c$ = 31 K. The agreement with experiment is encouraging.

At temperatures close to the Curie temperature the calculated curves (e.g., 27 K) show more intense shoulders to the spectrum than is in fact observed. This is in the opposite sense to any experimental saturation effects. The main contributions to the spectrum are from $Eu^{3+}$ ions with 6(61%), 5(32%), and 4(7%) NN $Ru^{5+}$ ions. It is possible to reproduce this effect by assuming that $B_{eff}(T)$ with 5 NN $Ru^{5+}$ ions is less than five-sixths of that for 6 NN $Ru^{5+}$ ions, etc. Alternatively, some degree of temperature-dependent spin canting caused by disorder would also produce varying reductions in the exchange field. We therefore feel that this is a real effect which is produced by the disorder as the Curie temperature is approached.

The spectrum of $Ba_2EuRuO_6$ (sample 6) at 4.2 K shown in Fig. 3 is consistent with a disorder of ≤5%, and with only a small NNN exchange interaction. The sharp outer components and the reduced intensity of the inner components supports this. A more intense central component seen in
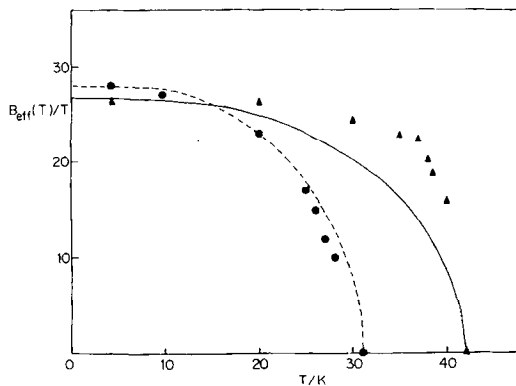


FIG. 7. The magnetic flux density for $Eu^{3+}$ ions with six NN sites occupied by $Ru^{5+}$ as a function of temperature in $Sr_2EuRuO_6$ (circles) and $Ba_2EuRuO_6$ (triangles). The calculated curves assume that the $Ru^{5+}$ exchange field follows the $S = \frac{3}{2}$ Brillouin function. The marked deviation in the barium compound is believed to be a result of spin canting.

sample 5 (not shown) was originally thought to be an impurity phase not visible in the X-ray spectrum. However, we now consider that this is probably due to a limited clustering of $Eu^{3+}$ ions in the perovskite phase which is removed by longer heating times. The temperature dependence in $Ba_2EuRuO_6$ is not the same as that found in the $Sr_2EuRuO_6$. The effective value of the magnetic flux density for six NN $Ru^{5+}$ sites differs markedly from the theoretical curve with $B_{eff}(0) = 26.8$ T and $T_c = 42$ K, and shows only a small decrease until 37 K. Even more remarkable is the dramatic increase in the relative intensity of the central components of the spectrum about 30 K even though the outer lines remain sharp. This effect does not appear to be due to any time dependence of the hyperfine spectrum as a whole, and was found to apply to both samples 5 and 6.

The most likely explanation for this curious behaviour is the onset of substantial spin-canting above 30 K, which is stronger in $Ba_2EuRuO_6$ than in $Sr_2EuRuO_6$. The cubic symmetry in $Ba_2EuRuO_6$ results in a low anisotropy at the $Ru^{5+}$ sites which facilitates misalignment of individual spins. The tetragonal distortion of $Sr_2EuRuO_6$ will result in greater anisotropy at the $Ru^{5+}$ site and a weaker tendency to show spin canting. A precedent for spin canting is known in the garnet system $\{Eu_3\}$ $[Sc_xFe_{2-x}](Fe_3)O_{12}$, where scandium substitution causes canting of the iron $d$-site spins and a partial collapse of the $^{151}Eu$ spectrum (15). The latter system is relatively easy to simulate because each $Eu^{3+}$ ion has only two exchange interactions with $Fe^{3+}$ ions. In the present instance the larger number of exchange interactions means that the effects of spin canting are more complex, and although it is clear that this mechanism could account for the observed anomalies, no attempt has been made to simulate this theoretically.

The calcium compound $Ca_2EuRuO_6$ is clearly very different from the other two. The $^{151}Eu$ spectrum at 4.2 K is not inconsistent with almost complete disorder, but the lack of fine structure makes it difficult to carry out a complete analysis. The field at $Eu^{3+}$ ions with six NN $Ru^{5+}$ ions is of the same order as in the Sr and Ba compounds. The spectrum also narrows considerably with increasing temperature until the ordering temperature of $T_c \simeq 18$ K is reached. Thus the degree of disorder decreases and the Curie temperature increases along the sequence Ca, Sr, Ba.

This detailed interpretation of the data considers the observed magnetic flux density as an essentially static quantity at any given site. It could be said that some of the features of the spectra are not inconsistent with superparamagnetic relaxation effects. However, it seems unlikely that superparamagnetism could be induced by the isolation of small clusters of magnetic atoms in $Sr_2EuRuO_6$ and $Ba_2EuRuO_6$ when the degree of disorder is so small; the effects should be greater in $Sr_2EuRuO_6$ and not as observed. Furthermore, there was comparatively little difference between samples of the same compound prepared under different conditions, and thus small-particle superparamagnetism also seems an unlikely explanation.

## Conclusions

The X-ray and $^{151}Eu$ Mossbauer data in combination allow several conclusions to be drawn regarding the nature of the three compounds. Prolonged annealing of $Ca_2EuRuO_6$ produces a cubic perovskite cell of lattice parameter $795 \pm 1.3$ pm. Long-range magnetic order takes place below $T_c \simeq 18$ K, but the $Eu^{3+}$ and $Ru^{5+}$ cations are highly disordered. $Sr_2EuRuO_6$ adopts a tetragonally distorted perovskite cell with $a = 796 \pm 1$ and $c = 787 \pm 1$ pm and has a Curie temperature of 31 K. The $Eu^{3+}$ and $Ru^{5+}$ cations show a considerable

degree of ordering, and less than 8% of the cations are on "wrong" sites. $Ba_2EuRuO_6$ has a face-centered cubic perovskite cell of lattice parameter $840.6 \pm 0.1$ pm and a Curie temperature of 42 K. Less than 5% of the cations are on "wrong" sites. However, the combination of a cubic lattice and partial disorder results in substantial spin canting of the $Ru^{5+}$ spins at temperatures immediately below the Curie temperature. This effect is considerably reduced in $Sr_2EuRuO_6$ because of the greater site anisotropy in the tetragonal lattice. In all three compounds the magnetic exchange between $Ru^{5+}$ ions takes place via the formally diamagnetic $Eu^{3+}$ ion by a mixing in of the low-lying magnetic excited states.

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