Magnetic Behavior of Europium Silicates
Using Nuclear Gamma Resonance Spectroscopy

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Dedicated to Prof. Dr. H. Maier-Leibnitz on the occasion of his 60th birthday

The ferromagnetic transition temperature, the quadrupole interaction, the hyperfine magnetic field, and the isomer shift have been measured in Eu$_2$SiO$_4$ and Eu$_3$SiO$_5$ using the 21.6 keV nuclear gamma resonance in $^{151}$Eu. The isomer shifts found ($-0.6$ mm/sec for Eu$_2$SiO$_4$ and $+0.1$ mm/sec for Eu$_3$SiO$_5$ against EuS) are less negative than the values typical for other ionic Eu$^{2+}$ compounds. The magnetic hyperfine fields (280 kOe for Eu$_2$SiO$_4$ and 240 kOe for Eu$_3$SiO$_5$) are much lower than the Eu$^{2+}$ free ion value. A brief qualitative discussion of these hyperfine parameters is given.

A rough correlation between the isomer shift and the transition temperature for various divalent Eu compounds is indicated. The effect of trivalent Eu impurities on lowering the Curie temperature of the silicates is demonstrated.

1. Introduction

The silicates of europium have been investigated recently for their structural, optical, magnetic, and luminescent properties. Amongst the known stable phases of the (EuO-SiO$_2$) system, the orthosilicate Eu$_2$SiO$_4$ and Eu$_3$SiO$_5$ exhibit ferromagnetic behavior inspite of being ionic transparent insulators. They have thus stirred considerable interest. Nuclear gamma resonance (NGR) is a powerful tool to probe the microscopic behavior of magnetic materials. In particular the 21.6 keV resonance in $^{151}$Eu has excellent characteristics for investigating both the magnetic and chemical nature of europium ions. In this contribution we report NGR measurements of the hyperfine parameters in these silicates over the temperature region from 77 K to 1.5 K. From this we deduce the ferromagnetic transition temperature, the low temperature hyperfine magnetic field, and the isomer shift. A brief qualitative discussion of the findings is given.

2. Crystal Structure

Both these silicates are structurally complex. Eu$_2$SiO$_4$ has either orthorhombic or monoclinic. Eu$_3$SiO$_5$ belongs to the tetragonal system with space group I4c2. The Eu$^{2+}$ ions have two site symmetries. While at both the sites the Eu$^{2+}$ ions are surrounded by distorted oxygen octahedra; the nearest and next nearest oxygen distances differ slightly for the two sites.

3. Experimental

Conventional experimental techniques of NGR spectroscopy have been adopted in the present investigation. All measurements were performed in transmission geometry with a 50 mCi source of $^{151}$SmO$_3$. The source was always kept at roughly the same temperature as the absorber. All samples investigated have been obtained from IBM-Laboratories where the compounds have been synthesized by solid-state reaction of EuO and Eu$_2$O$_3$.
and SiO₂ in a hydrogen atmosphere. The resulting crystals were crushed by us into fine powder and absorbers of about 5 – 10 mg/cm² thickness were formed by spreading the powder into a disc-shaped lucite container. This then was sealed in an inert and dry atmosphere.

The NGR spectra were analyzed on an IBM 360/75 computer using a least-squares fitting routine discussed earlier. All isomer shifts are given with reference to a standard EuS absorber.

4. Results

The resonance spectra of both silicates at 77 K showed a strong absorption centered around −0.5 mm/sec. This isomer shift (IS) is representative of a divalent europium ion. The width of this absorption peak is broader than that obtained with an equally thick paramagnetic EuS absorber using the same source. Since the Eu²⁺ ions in both silicates have a low site symmetry, the observed broadening is considered to be due to quadrupole interactions. Unfortunately the ratio of the nuclear quadrupole moments of the ground state and the 21.6 keV excited state is such that pure quadrupole spectra are commonly unresolved for this resonance. The computer analysis gives an interaction energy of \( e^2 q Q = -12 \text{ mm/sec} \) in Eu₂SiO₄. A somewhat larger value was obtained for Eu₃SiO₅. However, in this compound Eu²⁺ ions occupy two sites with different symmetries and one actually should fit two different quadrupole spectra to the experimental spectrum. In view of the poor resolution, this was not attempted and only the average value for \( e^2 q Q \) was derived. The results are given in Table 1.

Table 1. Curie temperatures and hyperfine interaction parameters for Eu Silicates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_c ) (pure sample) K</th>
<th>( T_c ) (our sample) K</th>
<th>Eu²⁺ (our sample) %</th>
<th>( e^2 q Q ) mm/sec</th>
<th>( H_{hf} ) kOe</th>
<th>Isomer shift (vers. EuS) mm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu₂SiO₄</td>
<td>9</td>
<td>5.2 ± 0.5</td>
<td>5</td>
<td>-12.0 ± 0.3</td>
<td>280 ± 5</td>
<td>-0.6 ± 0.1</td>
</tr>
<tr>
<td>Eu₃SiO₅</td>
<td>19</td>
<td>11.5 ± 0.5</td>
<td>8</td>
<td>-19.0 ± 10</td>
<td>240 ± 10</td>
<td>+0.1 ± 0.15</td>
</tr>
</tbody>
</table>

\( a \) From Ref. 3; \( b \) from Ref. 12; \( c \) from spectrum taken at 77 K; \( d \) average value for both lattice sites; 

In addition to the Eu²⁺ absorption a weak resonance is found near +13.3 mm/sec. This corresponds to a trivalent europium impurity present in these compounds. In accordance with Ref. 3 this is to be expected by the method of preparation used. Because of the large differences in the IS between Eu²⁺ and Eu³⁺ ions, the NGR of ¹⁵¹Eu provides a unique non-destructive method to estimate the Eu³⁺ content in Eu²⁺ compounds. Assuming the Debye-Waller factor (which gives the strength of the reso-
nance absorption) to be the same for both the impurity Eu³⁺ and the host Eu²⁺ ions, we have estimated the Eu³⁺ content in our samples. The results are also given in Table 1.

Both Eu₂SiO₄ and Eu₃SiO₅ are known to be ferromagnetic¹ at 4.2 K. The transition temperatures are reported⁴ to be 7 K and 19 K, respectively. The NGR spectra measured well below the Curie temperature \((T_C)\) showed a well developed hyperfine (hf) magnetic splitting. Close to the transition temperature the hf magnetic field \((H_{hf})\) decreases rather rapidly and becomes zero at \(T_C\). In Fig. 1 we show spectra taken around \(T_C\) for Eu₂SiO₄. By plotting \(H_{hf}\) versus \(T\) and extrapolating for \(H_{hf}=0\), we find \(T_C\) to be \((5.2\pm0.5)\) K for Eu₂SiO₄ and \((11.5\pm0.5)\) K for Eu₃SiO₅.

Resonance spectra measured at 1.6 K were analyzed using a Hamiltonian for an axially symmetric quadrupole interaction \((\eta=0)\) and with the direction of \(H_{hf}\) along the principal efg axis \((\Theta=0, \Phi=0)\). Because of the low symmetry of the Eu²⁺ ions in the silicates these assumptions are surely an oversimplification. On the other hand, a fit with the correct Hamiltonian contains too many free variables and the fitting routine is unable to find a reproducible set of minimized parameters. Using a simulation program for the calculation of theoretical hf spectra we have shown earlier⁸ that the structure of the spectrum is not sensitive to the chosen values of \(\Theta\) and \(\Phi\), provided \(gH_{hf}\gg e^2\mathbf{q}Q/4I(2I-1)\).

Furthermore, under this condition, the influence of \(\eta\) is barely noticeable, in particular for values of \(\eta<0.4\). From these simulations it is seen that using the simple Hamiltonian described earlier, the deduced value of \(H_{hf}\) is correct within the experimental limits of error. But the number for \(e^2\mathbf{q}Q\) returned by the fit is in general smaller than its actual value. This effect is clearly seen in our results, which give a value of \(e^2\mathbf{q}Q=-4.3\) mm/sec from the fitting of the magnetic spectrum of Eu₂SiO₄. This number is about 30\% of the value deduced from the pure quadrupole spectrum (Table 1). We take this as evidence that \(H_{hf}\) makes an angle with the principal efg axis. The spectrum of Eu₃SiO₅ did not show this effect quite so pronounced, but its analysis is further complicated by the presence of two lattice sites for Eu²⁺. However, the spectra taken well below \(T_C\) clearly show that the magnetic hf fields must be nearly the same for both sites. The value for \(H_{hf}\) given in Table 1 is an average. From the observed line width we can set a limit of 10\% for the difference in \(H_{hf}\) for the two sites. No difference in IS within the experimental errors was found for the resonances above and below the Curie points.

5. Discussion

The nature of the exchange interaction in divalent europium compounds has at present been discussed mainly for the chalcogenides⁸. The molecular field model is used in deriving the coupling between the nearest neighbors \((J_1)\) and the next nearest neighbors \((J_2)\). The relative strength of \(J_1\) compared to \(J_2\) determines the basic magnetic behavior since \(J_1\) is a ferromagnetic coupling while \(J_2\) is antiferromagnetic. A 4f-5d hybridization leads to an overlap of the orbitals of nearest neighbors and produces \(J_1\). The antiferromagnetic coupling is due to superexchange via the \(p\) orbitals of the anions. Thus ferromagnetism \((J_1\gg J_2)\) is observed if the energy of promoting 4f electrons into 5d orbitals is small and if the 5d-4f overlap is large. The first condition is mainly governed by the lattice parameter, the second by the symmetry of the anion field. In the silicates the Eu²⁺ are surrounded by a distorted oxygen octahedron which presumably puts the \(t_{2g}-5d\) orbitals lower in energy than the \(e_g-5d\) orbitals. A simple minded comparison between the chalcogenides and the silicates thus predicts a rather high \(T_C\) for the latter⁴. However, the lowering of octahedral symmetry (distortion) will lift the degeneracy of \(t_{2g}\) orbitals, which in turn will reduce the \(5d-4f\) overlap and thereby lower the transition temperature.

The electronic structure of the cation \((\text{Eu}^{2+})\) is reflected in the observed IS. From the above discussion it is obvious that there should be some relation between the IS, the transition temperature, and the type of ordering. We have plotted in Fig. 2 the IS of non-metallic compounds of Eu²⁺ versus the transition temperature as they are reported in the literature⁹. From this it can be seen that the Eu²⁺ compounds with higher transition temperature tend to show a higher s-electron density at the nucleus.


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Fig. 2. Isomer shift of various non-metallic Eu²⁺ compounds plotted against their magnetic transition temperatures. Most of the data are taken from Ref. 9.

The antiferromagnetic ionic compounds like EuSO₄ are expected to come closest to a pure 4f⁷ configuration. The promotion of 4f electrons into 5d orbitals will increase the charge density at the nucleus, since the shielding of 6s electrons by 5d electrons is only about 30% of that by 4f electrons. Using a Hartree-Fock self-consistent field calculation¹⁰ it should be possible to estimate the amount of 5d hybridization. However, we have refrained from doing so, because the effect of increasing 6s overlap with decreasing lattice parameter will also markedly influence the IS. Both these contributions are inseparable. The silicates in question show IS which are in general agreement with this qualitative picture. Although the silicates are usually termed “ionic compounds”, it should be noted that their IS are less negative than the ones of the more typical ionic compounds (like EuSO₄ and EuF₂) and more in the region occupied by the chalcogenides. In addition, the hf fields found in both silicates are markedly lower than the value reported¹¹ for the free Eu²⁺ ion (−341 kOe). In contrast, the hyperfine fields of the ionic Eu²⁺ compounds (EuSO₄, EuF₂ etc.) are all rather close to the free ion number⁹. In the silicates an additional positive field, produced either by the dipolar contribution or by the 5d electrons, thus reduces the observed $H_{hf}$.

The values for $T_c$ reported here are somewhat lower than those given by KALDIS et al.³ and SHAFER¹². This lowering of $T_c$ can be attributed to the magnetic dilution of our samples by the non-magnetic Eu³⁺ ($^{6}F_0$) impurity ions. The estimated Eu³⁺ content of our samples is 5% in Eu₂SiO₄ and 8% in Eu₃SiO₅ (see Table 1). This finding is in agreement with an earlier report by McGUIRE and SHAFER¹³, who give $T_c = 4$ K for a sample of Eu₃SiO₅ containing roughly 20% Eu³⁺ impurities.

Acknowledgement

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¹⁰ G. K. SHENOY and G. M. KALVIUS, unpublished.