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ELECTRONIC, MAGNETIC AND STRUCTURAL PROPERTIES OF AMORPHOUS Eu$_{80}$Au$_{20}$ ALLOYS FROM HYPERFINE INTERACTIONS AT EUROPIUM

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Abstract. - Amorphous Eu$_{80}$Au$_{20}$ has been investigated by means of Mössbauer spectroscopy and NMR at $^{151}$Eu. A large electric field gradient (EFG) is detected. The EFG and isomer shift at Eu$^{2+}$ ions reveal unusually large temperature dependences between 4.2 and 245 K. This feature is tentatively attributed to tunnelling states, typical of amorphous materials. All the results are consistent with a strong structural short range order. The alloy orders asperomagnetically below $T_c=85$ K. The spontaneous magnetization, the hyperfine field distribution and the reduced magnetization temperature dependence are consistently discussed in terms of distributions of moments directions and of exchange interactions.

INTRODUCTION

Electronic and magnetic properties of amorphous alloys are closely connected with the structural and chemical short range order [1, 2]. Therefore, combined macroscopic (magnetization measurements [3]) and microscopic (Mössbauer spectroscopy and NMR) investigations are powerful tools for understanding the magnetic properties. The series of a-RE$_{80}$Au$_{20}$ alloys is particularly attractive because magnetic properties and crystal field effects vary with RE element, whereas one expects the structural short range order to be roughly constant on the basis of the strong similarities between RE - Au phase diagrams [4]. In these a-RE$_{80}$Au$_{20}$ alloys, only the RE atoms carry a magnetic moment, while the Au atoms are non-magnetic. The present paper is devoted to the study of a-Eu$_{80}$Au$_{20}$ which is an exemplary system in view of the following features : a) Eu is divalent; thus, anisotropy and crystal field are negligible b) Eu nuclei are suitable for both Mössbauer and NMR spectroscopies c) this amorphous material is magnetically ordered.

EXPERIMENTAL RESULTS

Bulk magnetization measurements were previously reported [3]. A Curie temperature of $T_c=85\pm5$ K was determined, consistently from AC-susceptibility and from Arrott plots. The saturation moment per Eu$^{2+}$ atom ($6.7\pm0.15$ $\mu_B$) is slightly reduced with respect to the theoretical value. The temperature dependence of the reduced spontaneous magnetization $M(T)/M_s$ is significantly flattened as compared to the $S=7/2$ Brillouin behavior (fig. 1).

Fig. 1 : Temperature dependence of magnetization of a-Eu$_{80}$Au$_{20}$ (circles) normalized to the spontaneous saturation magnetization, compared to Brillouin function (dashed line). The solid line corresponds to a calculation with $a_i$ and $J_{ij}$ distributions.

$^{151}$Eu Mössbauer spectroscopy confirms the ordering temperature : indeed, the paramagnetic absorption spectra broaden suddenly below $92\pm5$ K. Above this temperature, spectra are satisfactorily fitted assuming single values for both isomer shift $\delta_{IS}$ and quadrupole interaction $e^2QQ$ (Table 1, fig. 2). In the fits, the linewidth was constrained to 2.7 mm/s. Fits are insensitive to an EFG asymmetry parameter and attempts of including distributions of either $\delta_{IS}$ or (and) $e^2QQ$ were unsatisfactory.
The value of $e^2\Omega Q$ is unusually large for the Eu$^{2+}$ configuration in an intermetallic [5] and the positive sign is unambiguous. Both $\delta IS$ and $e^2\Omega Q$ display very large reversible temperature dependences (Table 1).

![Figure 2: $^{155}$Eu Mössbauer spectra of a-Eu$_8$Au$_2$O$_{19}$ at 185(a) and 4.2 K (b). Fits are represented by solid lines.](image)

**Table 1**: $^{155}$Eu Mössbauer hyperfine parameters. Errors on last figure in parentheses.

<table>
<thead>
<tr>
<th>Temperature ($T$)</th>
<th>$\delta IS$ (mm/s) at 300 K</th>
<th>$e^2\Omega Q$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>245</td>
<td>$-10.0 (2)$</td>
<td>$+315 (6)$</td>
</tr>
<tr>
<td>185</td>
<td>$-9.6 (1)$</td>
<td>$+278 (6)$</td>
</tr>
<tr>
<td>100</td>
<td>$-9.3 (1)$</td>
<td>$+261 (4)$</td>
</tr>
<tr>
<td>4.2</td>
<td>$-8.3 (2)$</td>
<td>$+270$ (constrained)</td>
</tr>
</tbody>
</table>

Notice that the temperature dependence of the average $H_{hf}$ follows the reduced magnetization.

![Figure 3: Hyperfine field distribution (arbitrary unit) at $^{155}$Eu in a-Eu$_8$Au$_2$O$_{19}$ at 4.2 K.](image)

Spin echo NMR measurements were carried out at 1.4 K on same samples. The frequency corrected spectrum arises mainly from $^{155}$Eu nuclei (Fig. 4). Signals corresponding to the $^{153}$Eu and $^{197}$Au isotopes are possibly detected on the low frequency side. $H_{hf}$ and $e^2\Omega Q$ values of 160 ± 5 kOe and 330 ± 70 MHz are deduced from numerical analysis of the high frequency spectral side ($^{155}$Eu). Owing to the large quadrupole interaction, the perturbation treatment used here is of limited validity; this explains the large unaccuracy in the determination of $e^2\Omega Q$. In any case, the agreement between the NMR and Mössbauer hyperfine parameters is very satisfactory and gives confidence in the independently concluded results.

**DISCUSSION**

The unique values (or narrow distributions) measured for both $\delta IS$ and $e^2\Omega Q$ indicate that fluctuations of local (chemical) environment of Eu atoms are small. Indeed, the hyperfine parameters of Eu in crystalline compounds are known to depend significantly on the number and the nature of neighbors [5-6].

The large EFG arises from charge disturbances caused by the asymmetry of the nearest neighbors atomic surrounding since Eu$^{2+}$ is an orbital $S$ state ion. Referring to the structural studies on a-La$_{80}$Au$_{20}$ [7], each Eu atom has on average 8 Eu and 3 Au atoms as nearest neighbors. The EFG axes are likely to be randomly distributed with respect to any macroscopic axis.
The temperature dependence of $\delta_{1S}$ between 4.2 and 245 K is unusually large (Table I). It exceeds by an order of magnitude the second order Doppler shift ($-6.6 \times 10^{-7}$ mm/s from 4.2 to 245 K). The hypothesis of an Eu fluctuating valence is ruled out by the sign of the temperature dependence of $\delta_{1S}$. This indicates a decreasing electron density at increasing temperature, whereas thermal excitation of an $\text{Eu}^{2+}$ state would induce an effect of opposite sign. Also, photoemission measurements [8] at 300 K confirm a pure $\text{Eu}^{2+}$ valence and the effective paramagnetic moment from the Curie-Weiss law is $8.2 \pm 0.2 \mu_B$/at, which is close to the $\text{Eu}^{2+}$ ionic value (7.94 $\mu_B$/at). The anomalous behaviour of $\delta_{1S}$ cannot either be accounted for by thermal expansion. Indeed, by reference to crystalline Eu systems, the volume expansion over this range of temperature should be roughly 15 % in order to account for the observed change of $\delta_{1S}$ [9].

We suggest tentatively that the anomalous thermal dependences of $\delta_{1S}$ and $e^2\gamma Q$ might be a specific consequence of the amorphous structure. Some properties of covalent glasses and of metallic amorphous systems (e.g. sound velocity, ultrasonic attenuation) have been explained in the frame of a two-levels-systems (TLS) model [10–13]. In the TLS, the elastic potential curve versus generalized coordinates of atoms presents several minima. Thus, inequivalent atomic positions can be occupied through a dynamic thermal process. Assuming that these inequivalent positions have slightly different structural environments, and therefore different $\delta_{1S}$ and $e^2\gamma Q$ values, it is expected that the time-averaged $\delta_{1S}$ and $e^2\gamma Q$ measured by Mössbauer spectroscopy may shift with changing temperature.

The saturation moment at 4.2 K, as obtained from an $1/H$ extrapolation, is $6.7 \pm 0.15 \mu_B$/Eu at. This rather low value for a $4f^7$ configuration can be interpreted as a result of misalignment of moments (asperomagnetism). The computation of the cone angle requires the knowledge of the saturation moment in case of perfect spin alignment. The moment of $\text{Gd}^{3+}$ is known to be $7.55 \mu_B$/at, which is interpreted as the sum of the $4f^7$ contribution ($7 \mu_B$) and of the $5d^{10}s^2$ conduction electrons contributions (0.55 $\mu_B$). A comparison of the 4.2 K high field isotherm curves of $\alpha$-$\text{Gd}_{80}\text{Au}_{20}$ and $\alpha$-$\text{Eu}_{80}\text{Au}_{20}$ shows that the moment of Gd exceeds by $0.15 \pm 0.05 \mu_B$ the one of Eu, under the reasonable assumption of identical magnetic structures. This difference originates from different conduction electron polarizations. Thus, Eu atoms should carry a moment of $7.3 \mu_B$. Consequently, the lowering of the macroscopic Eu moment by asperomagnetism is $0.6 \pm 0.1 \mu_B$/at.

The whole of the present magnetization and hyperfine field distributions can well be accounted for assuming such an asperomagnetic order [2]. At low temperature, spin directions are not collinear, owing to structural disorder which induces canting of the local easy axes of magnetization. However, this anisotropy is weak because $\text{Eu}^{2+}$ is an $S$-state ion. Let $\alpha_i$ be the angle between the spin $\text{S}_i$ and the reference axis defined by the macroscopic magnetization direction, and let $J_{ij}$ be the exchange interaction between $\text{S}_i$ and $\text{S}_j$; the Heisenberg Hamiltonian expresses as:

$$\mathcal{H} = - J_{ij} \langle \text{S}_i^z \rangle \langle \text{S}_j^z \rangle \cos(\alpha_i - \alpha_j)$$

(1)

The reduction of saturation moment per $\text{Eu}^{2+}$ atom is understood assuming a gaussian distribution of
with a FWHM equal to 60°. The 6s net density being constant, it is reasonable to assume that $J_{ij}$ has a narrow (gaussian) distribution around the mean value.

The hyperfine field at Eu nuclei arises from three main contributions:

$$H_{hf} = H_{cp} + H_{op} + H_n$$

(2)

$H_{hf}$ is the core polarization, which reflects the susceptibility of the inner shells via intra-atomic exchange with the localized moment. $H_{op}$ is the ion's own polarization of the 6s electrons. According to Nowik et al [14], the 6s polarization is proportional to the 6s net density and thus, a monotonous correlation between $H_{op}$ and $\delta_{IS}$ is observed. In this picture, if the $H_{hf}$ distribution would only arise from $H_{op}$, the $\delta_{IS}$ distribution should be several mm/s wide. This is not experimentally observed. Therefore, we conclude that, in a-Eu$_{80}$Au$_{20}$, both $H_{op}$ and $H_{cp}$ are roughly constant. $H_{cp}$ is the contribution of the neighbors to $H_{hf}$ at the central site. The $H_{hf}$ distribution must arise from this term. Under the assumption that the $H_{hf}$ distribution reflects the distribution of exchange field, the Mössbauer probability $P(H_{hf})$ (which is also consistent with NMR data) is interpreted as resulting from both $\alpha_i$ and $J_{ij}$ distributions. The gaussian distribution of $\alpha_i$ leads to an exchange field distribution of truncated parabolic shape. The gaussian $J_{ij}$ distribution (FWHM = 25°) is narrow, in relation with the well defined $\delta_{IS}$. Assuming that $\alpha_i$ and $J_{ij}$ are independent variables, $P(H_{hf})$ will be given by a convolution of these two distributions. Since long range magnetic interactions are dominant ($T_c$ is well defined), we have computed the reduced saturation magnetization versus $T/T_c$ in a mean field approximation taking both $\alpha_i$ and $J_{ij}$ distributions into account. The agreement with experimental data is indeed satisfactory (fig. 1). A Mössbauer investigation of the thermal variation of the width of $P(H_{hf})$ is impracticable because of fitting ambiguities above 40 K. Such data would have allowed to confirm that the main part of the magnetic coupling has long range character [15].

**CONCLUSION**

The magnetic properties of a-Eu$_{80}$Au$_{20}$ are consistently depicted assuming a narrow distribution of exchange interaction between the localized moments, which are amperomagnetically ordered at low temperature. These magnetic properties, the unique value of the isomer shift and of the quadrupole interaction for all the Eu$^{2+}$ atoms confirm that there is a strong short range order. The isomer shift and the quadrupole interaction display anomalously large reversible temperature dependences, which are tentatively described in terms of a two-levels model, characteristic of amorphous states. Mössbauer spectroscopy experiments at both rare earth and gold atoms in other a-RE$_{80}$Au$_{20}$ are in progress. These combined studies should provide detailed information with respect to magnetic order, short-range order and crystal field effects in such amorphous intermetallics.

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