

Hyperfine Fields and Isomer Shifts in Magnetically Ordered Europium Compounds

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The Mössbauer technique was employed to study hyperfine fields in several ordered divalent europium compounds at low temperatures. The intermetallics EuCu_2 , EuAl_2 , and EuAl_4 were ordered at helium temperatures and the observed fields and isomer shifts were 189(8) kOe, -0.88 cm/sec; 278(8) kOe, -0.97 cm/sec; and 290(8) kOe, -1.14 cm/sec, respectively. Comparison of these results and previous measurements with EuO , EuS , and Eu metal indicates a possible correlation between isomer shift and internal field. With the exception of EuCu_2 the internal fields increase with increasing magnitude of isomer shift. Interpretation of this trend with a core polarization model yields a value of 120 ± 20 kOe for the field per $6s$ valence electron.

SEVERAL Mössbauer experiments have shown that divalent ^{151}Eu ions in different compounds display large and varied isomer shifts relative to an Eu_2O_3 source.¹⁻⁴ In addition, the europium chalcogenides and several intermetallic systems are ordered at low temperatures. In this paper we report measurements of "saturation" hf interactions (hfs) and isomer shifts (IS) in a number of compounds and discuss the possibility of a correlation between these parameters. A core polarization model leading to a correlation of hfs and IS and previously applied to Eu metal, EuO , and EuS is also applicable to EuAl_2 and EuAl_4 . However, such a simple picture is not applicable without modification to similar measurements in EuCu_2 . Recently, Winkler⁵ has also discussed core polarization in europium, and Danon and de Graaf⁷ have noted an apparent correlation between isomer shifts and bulk magnetic properties.

Sources of ^{151}Gd or ^{151}Sm in oxide form were employed. Isomer shifts were determined at 77°K ; the magnetic systems were ordered at helium temperatures. The experimental data and other pertinent information are summarized in Table I.

In divalent europium compounds the hyperfine fields arise from polarization of s electrons (owing to the paramagnetic $4f$ electrons) which yield a resultant field at the nucleus via the Fermi contact interaction. Isomer shifts in $^{151}\text{Eu}^{2+}$ are proportional to the difference

between electron densities at absorber nuclei and similar densities in source nuclei,

$$\text{IS} \propto (|\psi(0)|_{\text{abs}}^2 - |\psi(0)|_{\text{source}}^2).$$

Because both hfs and IS are functions of $|\psi(0)|^2$ it is reasonable to consider the possibility of a correlation between the two parameters.

For Eu^{2+} compounds we write the configuration as $4f^7 5s^2 6s^x$ to emphasize the shielding (at the nucleus) of the outer $5s$ electrons by $4f$ electrons.⁸ In the experiments the source, Eu^{3+} , $4f^6 5s^2 6s^0$, has larger $5s$ electron density at the nucleus than Eu^{2+} , $4f^7 5s^2 6s^x$ ^{4,5}; all the divalent compounds studied showed large negative IS. For example, in ionic EuF_2 with Eu^{2+} , $4f^7 5s^2 6s^0$, the shift was -1.5 cm/sec; for intermediate compounds $4f^7 5s^2 6s^x$ shifts with magnitudes less than 1.5 cm/sec are expected as $0 \leq x \leq 2$. That is, as $6s$ electrons (valence or conduction) are added, the charge density at the nucleus increases and $|\text{IS}|$ decreases.

Consider now the spin density yielding a hyperfine field H_{eff} which may be approximated as a constant "core" or non- $6s$ contribution and a varying contribution from the $6s$ electrons: $H_{\text{eff}} = H_{\text{core}} + H(6s^x)$. Theoretical calculations indicate the two contributions to the field are oppositely directed.⁹ Thus, if the polarizability remains constant, H_{int} must decrease as $x \rightarrow 2$. It is suggested below that in EuCu_2 the polarizability is affected by the copper $3d$ and $4s$ bands and the assumption made above fails in such cases. However, the approximation of constant polarizabilities should be satisfied in the other systems studied. Hence we write

⁸ L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

⁹ R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 2027 (1961).

¹ P. H. Barrett and D. A. Shirley, *Phys. Rev.* **131**, 123 (1963).

² P. Kienle, *Rev. Mod. Phys.* **36**, 372 (1964).

³ P. Brix, S. Hüfner, P. Kienle, and D. Quitman, *Phys. Letters* **13**, 140 (1964).

⁴ D. A. Shirley, R. B. Frankel, and H. H. Wickman, *Rev. Mod. Phys.* **36**, 392 (1964). An obvious error occurred in this abstract: in line 12, "Divalent Eu^{2+} " should read "Trivalent Eu^{3+} ."

⁵ H. H. Wickman, Ph.D. thesis, Berkeley (1964), unpublished.

⁶ R. Winkler, *Z. Physik* **184**, 433 (1965).

⁷ J. Danon and A. M. de Graaf (private communication).

TABLE I. Isomer shifts and magnetic interactions in several europous compounds.

	Transition temperatures ($^{\circ}\text{K}$)	-IS (cm/sec)	H_{eff} ($^{\circ}\text{K}$) (kOe)	Other measurements (of IS)
EuO	69 (T_c)	1.15(3)	300 \pm 8(4.2)	
EuS	16.3 (T_c)	1.26(3)	331 \pm 10(4.2)	1.17(3) Ref. 3
EuSe	7 (T_c)	1.26(3)	331 \pm 10(4.2)	1.22(2) Ref. 3
EuF ₂	2 (T_c)	1.50(3)		
EuCu ₂	20 > T_n > 4.2	0.88(3)	196 \pm 10(1.8)	
EuAl ₂	77 > T_n > 20	0.97(3)	278 \pm 10(1.8)	
EuAl ₄	\sim 6	1.14(3)	290 \pm 10(1.8)	
Eu metal	87 (T_n)	0.82(3)	265 \pm 10(4.2)	

$H_{\text{int}} = H_{\text{core}} + \alpha x$ and for isomer shifts a similar expression, $\text{IS} = \text{IS}_{\text{core}} + \alpha' x$. These expressions combine to yield a linear relation $H_{\text{int}} = \beta \text{IS} + \gamma$ between hfs and IS. In Fig. 1 this relation is tested by plotting H_{eff} vs IS. The dotted line in Fig. 1 represents a linear approximation to the data and yields the constant β , i.e., the field per unit isomer shift which is directly proportional to the number of 6s electrons, as shown below. Thus the field per 6s valence or conduction electron is

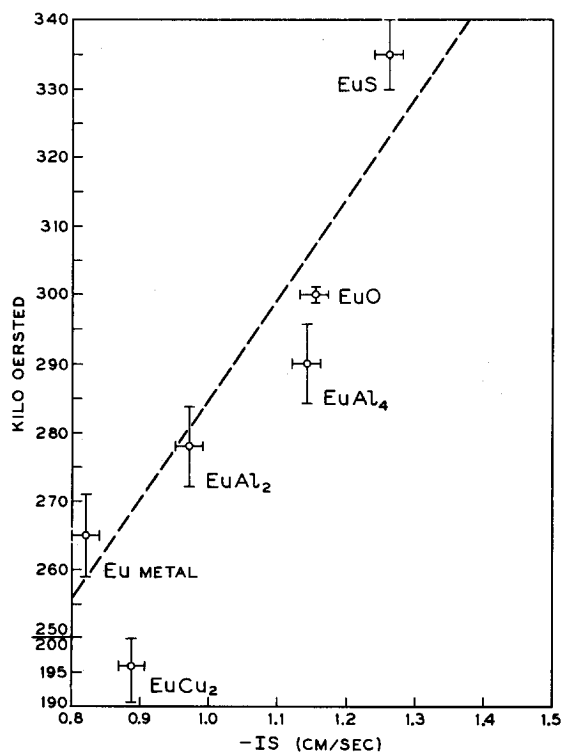


FIG. 1. Plot of H_{eff} vs IS in ordered europium compounds. Note the different scale for EuCu₂.

found to be 120 \pm 20 kOe. This is in good agreement with $H_{\text{eff}}(\text{EuAl}_2) - H_{\text{eff}}(\text{GdAl}_2) = 110$ kOe, where the two compounds differ in one conduction electron.¹⁰ Comparing this field with that of an atomic europium 6s electron we find a polarization 2.5%. Despite the approximate nature of the core polarization picture, the reasonably good correlation found here suggests the model has meaning. The obvious exception is EuCu₂ where more complex interactions are evidently in effect.

Methfessel had discussed the many types of magnetic interaction possible in lanthanide systems.¹¹ While the core contribution may be altered via indirect superexchange, it seems more likely that the interaction of the Eu 6s electrons with 3d and 4s bands in copper destroys the constant polarizability assumption, which is more tenable with diamagnetic cations.

An immediate deduction from Fig. 1 is the "core" polarization field in the absence of 6s electrons; this is $H_{\text{core}} = 355 \pm 20$ kOe, in agreement with the value 340 kOe obtained by Blumberg and Eisinger from ESR measurements with Eu²⁺; CaF₂.¹²

Finally, we derive a relation between the 6s character of europium compounds as a function of their chemical shift. The two constants in the equation $\text{IS} = \text{IS}_{\text{core}} + \alpha' x$ may be estimated by using $\text{IS} = 1.5$ cm/sec, when $x = 0$, and the relation between hf field and isomer shift in free europium atoms where $H_{\text{eff}} = 70$ kOe and $x = 2$, which implies $\text{IS} = 0.4$ for the free atom. This method was used, for example, to estimate the number of 6s valence electrons in Eu metal¹³ and more recently Brix *et al.* have used similar ideas to include other rare-earth ions.³

¹⁰ J. I. Budnick, R. E. Gegenwarth, and J. H. Wernick, *Bull. Am. Phys. Soc.* **10**, 317 (1965).

¹¹ S. Methfessel, *Z. Angew. Phys.* **18**, 414 (1965).

¹² W. E. Blumberg and J. Eisinger, *Bull. Am. Phys. Soc.* **6**, 141 (1961).

¹³ D. A. Shirley, *Rev. Mod. Phys.* **36**, 339 (1964).