ON THE CORRELATION BETWEEN THE MOSSBAUER PARAMETERS
AND THE MAGNETIC PROPERTIES OF EUROPIUM CHALCOGENIDES

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A possible correlation between Anderson superexchange and Mossbauer parameters (isomer shifts and hyperfine fields) is presented and applied to divalent Europium compounds.

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In this note we intend to discuss, in the light of recent developments, how the magnetic properties can be correlated to the measured Mossbauer parameters of EuO, EuS, EuSe and EuTe.

In table 1 we give the hyperfine fields [1] and the isomer shifts [2] relative to Eu_2O_3, at room temperature obtained by Mossbauer measurements, and the paramagnetic Curie temperatures [3] of these salts. These results imply that the total s-electron density at the Eu nucleus decreases while the spin

density passes through a maximum on going from EuO to EuTe. Recent band calculations [4,5] show that these salts are insulators with a valence band of p-character and a predominantly d-character conduction band, and an empty f↓ narrow band. Since no s-like states are present in the valence and in the lowest conduction bands, it seems difficult to discuss Mossbauer parameters in terms of 6s electrons, as it has been guggested [6].

The changes in isomer shift and hyperfine fields may be connected to inner shell screening [7,8] and core polarization [9] respectively.

Starting from inner shell screening and using chemical bonding arguments Danon and de Graaf [10] were able to point out a correlation between isomer shift data and the bulk magnetic properties of these salts.

The behaviour of the magnetic properties can be understood as follows: the Eu^{++} ions are coupled by two mechanism [11,12] a Bloembergen-Rowland (B-R) type of indirect interaction which tends to ferromagnetism and kinetic exchange (Anderson's super-exchange) which is antiferromagnetic. On going from EuO to EuTe the effect of kinetic exchange becomes gradually more important while the indirect interaction diminishes, thus finally making EuTe antiferromagnetic. The main point of this note is to ascribe to this increasing kinetic exchange a central role in the variation of Mossbauer parameters. It should be mentioned that the B-R interaction, provides only a negligible contribution to the inner shell

effects.

Kinetic exchange originates essentially in two effects [13]:

i) The off-diagonal matrix elements of the Coulomb inter-action introduce a quasi-particle character in the f-electrons due to the mixing with the valence and conduction bands.

ii) A second order calculation of the Coulomb interaction between these quasi-particles gives the coupling between neighbouring Eu^{++} ions.

The important point here is precisely the quasi-particle character of the f-electrons, given in second quantization form by:

$$S^+_{k,\uparrow} = C^+_{k,\uparrow}(f) - \sum_{k',k''} \frac{J^{(d)}_k(k',k'')}{E_d(k',k'') - E_p(k')} C^+_{k'',\uparrow}(f) \ C^{+(d)}_{k+k'-k'',\uparrow} \ C(p)_{k',\uparrow} -$$

$$- \sum_{k',k''} \frac{J^{(f)}_k(k',k'')}{E_{f\downarrow}(k'') - E_p(k')} C^+_{k'',\downarrow}(f) \ C^{+(f)}_{k+k'-k'',\uparrow} \ C_{k',\downarrow}(p) \tag{1}$$

where $J^{(i)}_k(k',k'')$ are the off-diagonal matrix elements of the Coulomb interaction (the notations are those of [13]).

It follows from (1) that the state $S^+_k |\psi_o\rangle$ ($|\psi_o\rangle$ being the one electron ground state defined in [4]) contains a $d\uparrow$-amplitude with spin parallel to the Eu^{++} ion band an $f\downarrow$ amplitude, both of which were absent in the one electron band calculation [4].

Two contributions are involved in (1): firstly one expects that $J_k^{(d)}(k', k'') > J_k^{(f)}(k', k'')$ along the series; secondly it has been shown [5] that the energy difference between p and $f\downarrow$ bands decreases along the series while the energy difference between p and d bands are expected to increase. These facts imply that in EuO and EuS the $d\uparrow$ amplitude dominates while for EuSe and EuTe the main contribution comes from the $f\downarrow$ amplitude.

This has two fundamental consequences: firstly, there is an increase in the screening of the nuclear potential for the inner s-electrons by these $d\uparrow$ or $f\downarrow$ electrons (inner shell screening effect) thus decreasing the s-electron density at the Eu nucleus; secondly, since the $d\uparrow$ amplitude dominates on going from EuO to EuS one has an increasing core polarization and consequently an increasing hyperfine field. For EuSe and EuTe the $f\downarrow$ amplitude dominates so one has a decrease in the hyperfine field. This qualitatively explains Table 1.

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TABLE 1

Paramagnetic Curie temperature (θ), isomer shifts (I.S.) relative to Eu_2O_3, at room temperature and hyperfine fields of Europium Chalcogenides.

	$\theta(^\circ K)$	I.S.(mm/sec)	H_{eff} (kOe)
EuO	80	-11.87 ± 0.11	300
EuS	19	-12.52 ± 0.08	331
EuSe	8	-12.65 ± 0.08	287
EuTe	-6	-12.87 ± 0.09	255

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REFERENCES:

1. H. H. Wickman and R. L. Cohen (private communication) and independently G. K. Shenoy (private communication).

2. G. Gerth, P. Kienle and K. Luchner, Phys. Letters 27A (1968), 557.

3. T. Kasuya and A. Yanase, Rev. Mod. Phys. 40 (1968) 684.

4. S. J. Cho, Phys. Rev. 157 (1967) 632.

5. S. J. Cho, Phys. Letters 29A (1969) 129.

6. F. A. Deeney, J. A. Delaney and V. P. Ruddy, Phys. Letters 25A (1967) 370.

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

8. R. Ingalls, Phys. Rev. 155 (1967) 157.

9. R. Watson and A. J. Freeman, Phys. Rev. Letters 277 (1961) 388E.

10. J. Danon and A. M. de Graaf, Phys. Chem. Solids 27 (1966) 1953.

11. A. M. de Graaf and R. M. Xavier, Phys. Letters 18 (1965) 225.

12. R. M. Xavier, Phys. Letters 25A (1967) 244.

13. A. Herpin, in Low Temperature Physics, ed. C. de Witt (Ecole d'Été de Physique Théorique, Les Houches 1961, Gordon and Breach Science Publishers, New York 1962) p. 307.

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