A FIRST ORDER TRANSITION IN EUROPIUM METAL

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RÉSUMÉ

Nous avons utilisé l'effet Mössbauer pour étudier en détail le comportement de l'interaction hyperfine (h. f.) pour le métal d'Europium près de la température d'ordre magnétique. L'amplitude de l'interaction magnétique hf étant essentiellement proportionnelle à l'aimantation du sous-réseau, nous avons mesuré la variation thermique de l'aimantation du sous-réseau dans un champ extérieur nul (la structure magnétique est en « spirale aplatie »). Les expériences montrent qu'à 88,6 °K, l'aimantation présente une discontinuité; l'aimantation varie entre 0,4 fois sa valeur à la saturation jusqu'à zéro. Les mesures du déplacement isomère entraîne sans équivoque, que les ions d'Europium sont dans l'état de valence $2+(^8S_{7/2})$ à toutes températures. Nous attribuons la disparition du champ hf à une transition de phase du premier ordre coïncidant avec la transition d'ordre magnétique, ceci n'avait jamais été observé. Des mesures récentes de chaleur spécifique justifient cette conclusion. A la transition apparaît une faible distorsion cristallographique (à partir de la structure b c c existant au-dessus de la température d'ordre), due à la magnétostriction. Nous avons aussi effectué les mesures de la dilatation thermique pour un échantillon polycristallin massif. Les résultats de ces mesures peuvent être reliés aux expériences déjà publiés sur les mesures de chaleur spécifique et sur les mesures à haute pression. Ceci permet de donner une explication au comportement anormal de la température d'ordre avec la pression. Finalement, la variation thermique de l'aimantation du sous-réseau, juste au-dessous de la transition, est analysée selon les théories de points critiques.

ABSTRACT

We have used the Mössbauer effect to study in detail the behavior of the hyperfine (hf) interaction in clean Eu metal near the magnetic ordering temperature. Since the size of the magnetic hf interaction is essentially proportional to the sublattice magnetization, we have thereby accurately measured the temperature dependence of the sublattice magnetization (the magnetic structure is "flat spiral") at zero applied field. The experiments show that at 88.6 °K, the magnetization falls discontinuously from 0.4 of the saturation value to zero. Isomer shift measurements establish unequivocally that the Eu ions are in the $2+(^8S_{7/2})$ valence state at all temperatures. We attribute the disappearance of the hf field to a previously unrecognized first order phase transition coincident with the magnetic ordering. Recent specific heat measurements support this conclusion. The transition appears to involve a small crystallographic distortion (from the b c c structure existing above the ordering temperature) due to magnetostriction. We have also performed thermal expansion measurements on a bulk polycrystalline sample. Results of those measurements can be related to previously published specific heat and high-pressure experiments. This leads to an explanation for the reported anomalous behavior of the ordering temperature with pressure. Finally, the temperature dependence of the sublattice magnetization just below the transition is analyzed in terms of critical point theory.

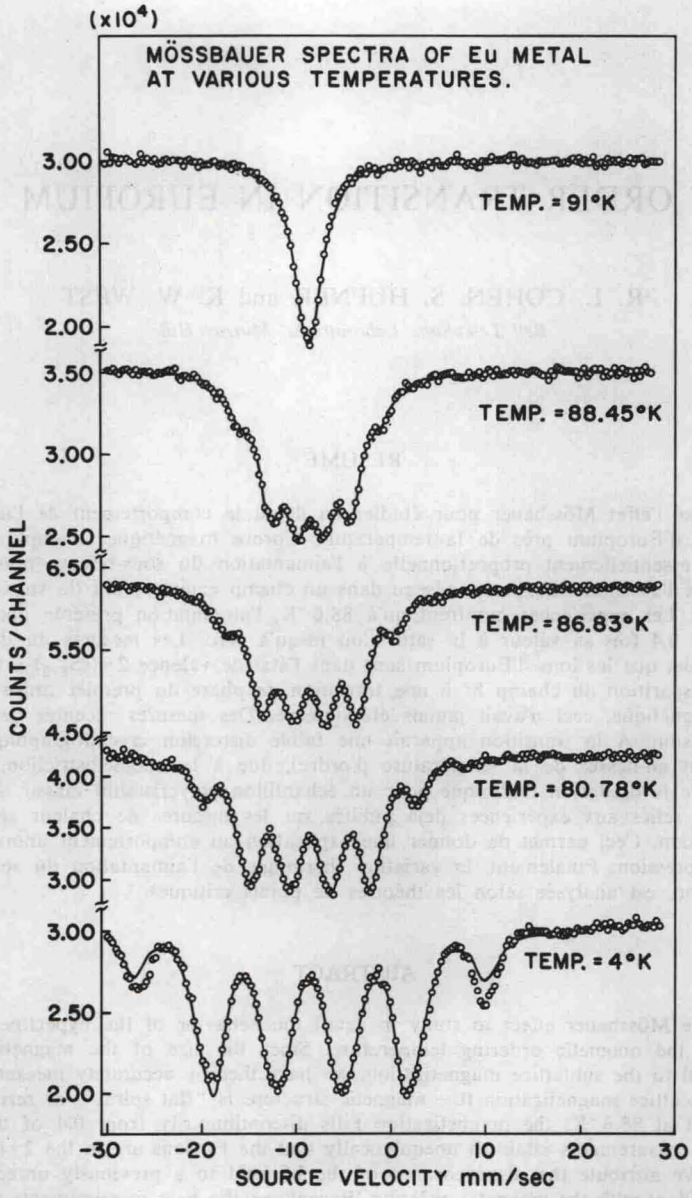

FIG. 1. — Spectra of Eu metal above and below T_t. The hfs below the ordering temperature is directly displayed and is proportional to the observed splitting. Each spectrum consists of 18 lines, not all of which are resolved. The solid line is the best fit to the observed points, using line positions and intensities constrained using the known properties of the Eu hf spectrum. The internal field is determined with a precision of about 0.1-0.2 % (1σ error limits). The differences between the data and least-squares curve (visible especially in the 5° data) result primarily from the fact that the absorber is so thick that saturation effects are significant, and the thin-absorber line intensities used for the theoretical curve are not exactly valid.

The magnetic ordering transition occuring in Eu metal at approximately 89 °K has been studied for many years by neutron diffraction [1], specific heat [2], Mössbauer effect [3, 4] and X-ray diffraction techniques [5]. The results have always been interpreted in terms of a normal

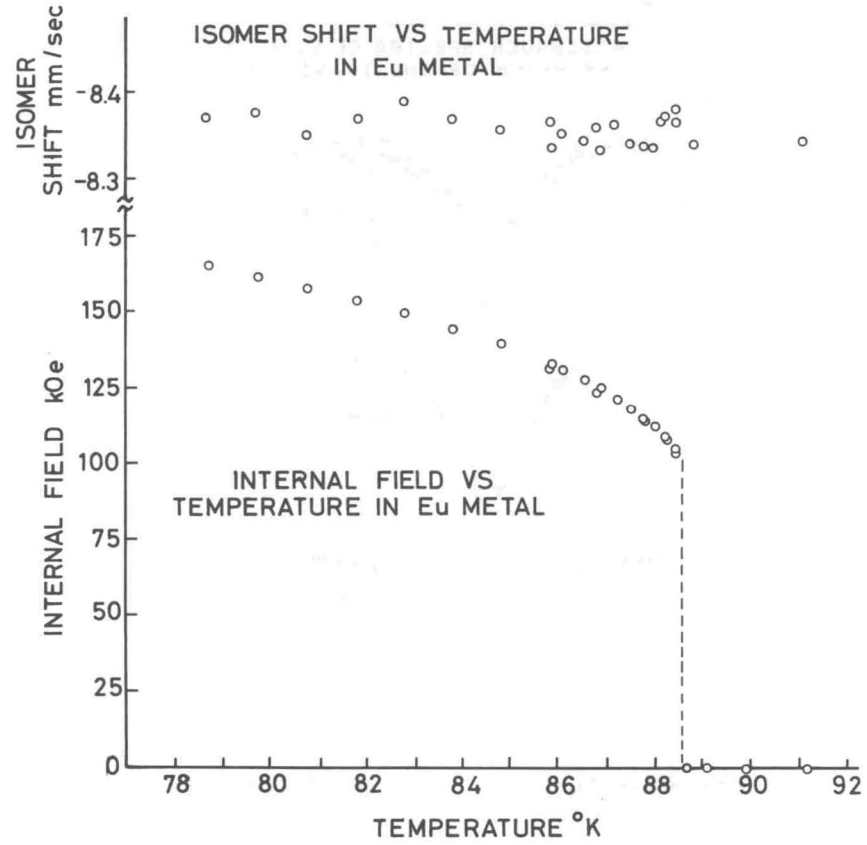

FIG. 2a. — Observed internal fields plotted as a function of temperature. Note the sudden drop of the field at T_t. The (1σ) error flags are about the size of the points.

FIG. 2b. — Observed isomer shifts as a function of temperature. Note that there is no substantial discontinuity at T_t. Isomer shift values are relative to an Eu_2O_3 absorber at 78 °K.

magnetic transition from the paramagnetic (bcc) phase existing at high temperatures to the spiral antiferromagnetic structure, below $\sim 89°$, established by neutron diffraction studies [1]. We present here unequivocal evidence from Mössbauer studies, that this transition is in fact of first order. Mössbauer effect measurements of the hyperfine structure in this material provide two useful pieces of information; the isomer shift, which is a sensitive indicator of the configuration of the rare earth ion, and the magnetic hyperfine interaction. The latter results from the interaction of the magnetic moment of the nucleus being studied (in this case, Eu^{151}) with the internal field at the Eu nucleus. In the case of Eu metal, the internal field comes primarily from core polarization resulting from the magnetically ordered 4f electrons, and is approximately proportional to the 4f moment [6]. Thus, Mössbauer effect hyperfine structure measurements serve to measure the sublattice magnetization. The measurements are performed at zero applied field (therefore eliminating problems due to the high anisotropy in this material) [7], and are essentially microscopic; i.e., if a range of hf fields is present in the sample, the spectrum will show that fact rather than simply indicating an average value for the field. In this respect, Mössbauer measurements tend to be, like the other resonance techniques, superior to bulk measurements such as susceptibility and dilatometry.

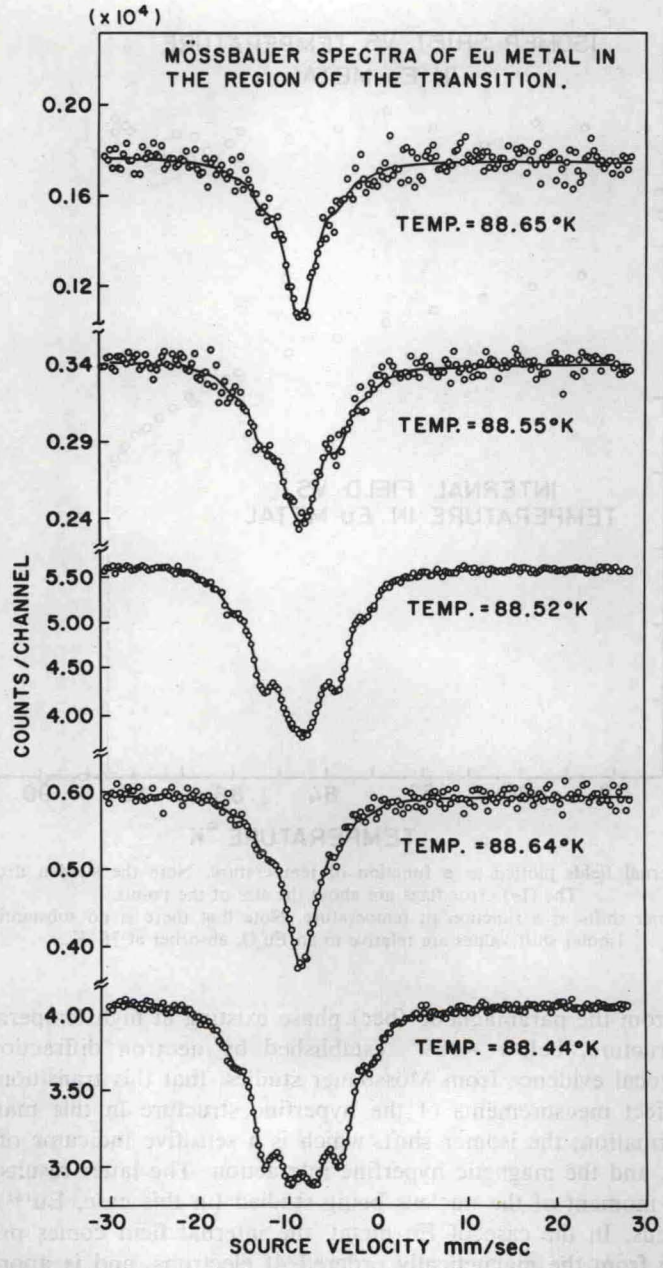

FIG. 3 .— Spectra of Eu metal in the temperature region of the phase transition. The spectra are shown (from the top) in order of the time at which they were taken. The solid line is the result of a least-squares fit assuming that the absorption resulted partly from a " split " spectrum like those in Figure 1 and partly from a single line. This is equivalent to the assumption that paramagnetic Eu (unsplit spectrum) and ordered Eu (split) coexist over a narrow temperature range. Parameters evaluated from the least-squares fits are plotted in Figures 4 and 5.

In brief, what the Mössbauer spectra show in this case, is that (see fig. 1) as the temperature is increased from 5 °K, the large hf splitting decreases as we approach 89 °K, but then (see fig. 2) suddenly vanishes at approximately 88.6 °K. This shows that the sublattice magnetization

goes suddenly from about 40 % of the saturation value to zero. The isomer shift remains essentially constant in passing through this transition (see fig. 2). Since the change in isomer shift between the $4f^6$ and $4f^7$ configurations is about 10 mm/sec, the observed constancy of the isomer shift absolutely excludes the hypothesis that the transition involves a 4f electron configuration change.

Further data on the detailed behavior of the spectrum in the temperature region about 88.6 °K is presented in figure 3. The success of the least-squares fits (described in detail in the figure caption) in describing the data in this temperature region shows that the observed spectra can be considered to arise from the simultaneous existence of two phases in the sample; a magnetically ordered one (with hyperfine splitting) and a paramagnetic one (which appears as the single sharp line in the center of the spectrum). In the temperature region from 88.4 °K to 88.8 °K, the relative proportions of the paramagnetic phase goes from $\sim$ 0 to 100 %.

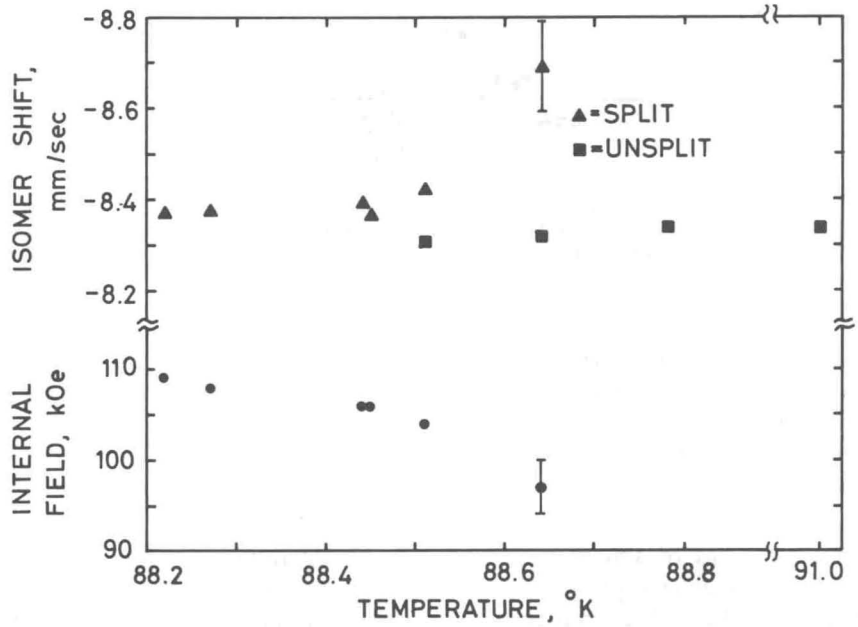

FIG. 4. — Internal fields and isomer shifts obtained from the least-squares fits shown in Figure 3. Error bars shown are 1σ; where no errors are indicated, they are about the size of the points. Note that the H_{int} of the split spectrum changes only very slightly in the transition region.

Fig. 4 shows some of the results of the least-squares fits to the spectra in this transition region. It is particularly significant here that though the fraction of paramagnetic material decreases toward 88.6 °K, the hf field decreases only very slightly. Thus, the Eu ions transform from a state with a substantial magnetization, to one with no magnetization, discontinuously. In fig. 5, the relative intensities of the two components of the spectrum are shown, with some runs being only ten minutes long. The excellent retracing of the points on increasing and decreasing temperatures shows that, within the accuracy of the measurements, no hysteresis is observed.

Our observation and interpretation of this magnetic ordering as a first order transition is actually supported by the specific heat measurements referred to earlier [2], which observed a sharp peak in the specific heat of Eu metal samples at about 88.6 °K. Both the sharpness and position of the specific heat peaks were observed to be strongly dependent on sample purity.

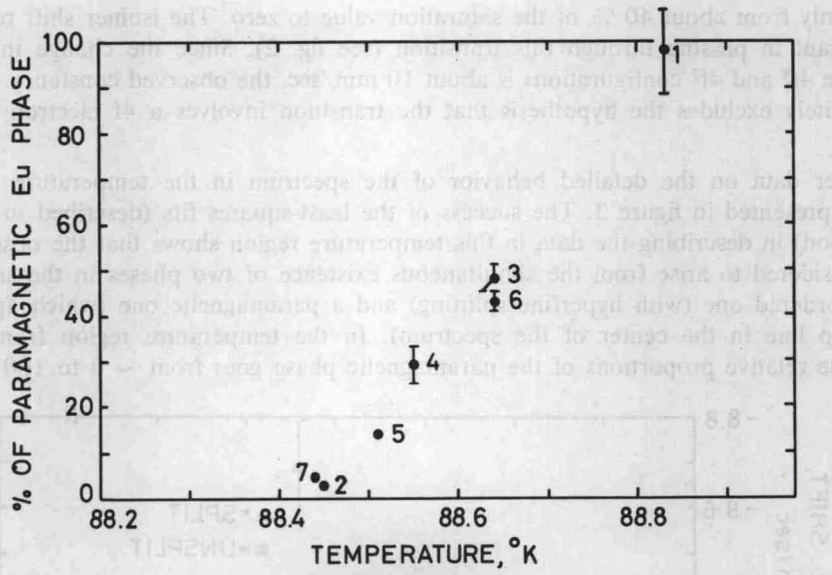

FIG. 5. — Ratio of the areas of the ordered and paramagnetic parts of the absorption spectra in the transition region. The points are numbered in the order in which the runs were made. The figure shows clearly the absence of hysteresis. The total transition width is about 0.3 °K. The transition width and temperature appear to lie intermediate between those for the two samples used in Ref. 2.

We hypothesize that the sharp transition we report was not observed earlier because of sample purity and temperature stability problems; the transition temperature is only about 1 °K below the magnetic ordering temperature obtained by extrapolating the data from 80° to 88° using a power law. Thus, if the sample is slightly non uniform or the temperature drifts slightly during the measurement, the sharp transition is blurred, and looks rather like a normal magnetic ordering.

There are two types of situations discussed in the literature which are used to develop models for first order magnetic phase transitions, which appear to be applicable to the analysis of the results reported here. The simpler of these, the "Isotropic magnetostriction" model developed by Bean and Rodbell [8], simply adds to the free energy of the magnetic spin system a term resulting from the mechanical (isotropic) distortion of the lattice. If the coupling between exchange and lattice constant is strong enough, compared to the stiffness of the lattice, the energy minimum criterion leads to a first order phase transition. For Eu, the appropriate parameters, compressibility and rate of change of "T_N" with lattice constant, are known [9], and it is easy to shown that the compressibility is at least one order of magnitude too small to account for the transition with this model. This lack of a large lattice volume change at the magnetic ordering is confirmed both by X-ray studies [5] and by our own dilatometry experiments.

A more complex theory developed by Lines [10] is similar in concept, but considers lattice distortion rather than isotropic compression. We think that in Eu metal the dependence of the exchange on the lattice parameters must be responsible for the occurence of the first order transition, and that, in principle, a theory as given by Lines and Jones [10] should also describe the present case. Due to the complex magnetic structure of Eu metal [1] no detailed theoretical treatment can be worked out with information presently available.

ACKNOWLEDGMENTS

We would like to acknowledge technical advice and comments from Dr. G. K. Wertheim concerning the particular problems of measurements, analysis, and discussion of critical point phenomena. We are greatly indebted to Dr. E. Helfand for theoretical discussions on the comparison of the results with critical point theory, and to Dr. M. E. Lines for helpful discussions on magnetostrictive first order transitions. We performed the thermal expansion measurements using equipment belonging to Dr. E. Fawcett, and we would like to thank him both for making the apparatus available and for helpful comments on the analysis of the data. The discussion reflects comments and suggestions by Dr. M. Blume.

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DISCUSSION

1. *Intervention de M. Kirchmayr :*

How closely does the internal field follow the macroscopic measurable magnetization ?

Réponse de M. Cohen :

Because of the extremely high magnetic anisotropy of Eu metal, bulk magnetization measurements are not a reasonable measurement of the ion moment. The hf field does follow the ion moment as measured by neutron diffraction.

2. *Intervention de M. Jones :*

Do you mean exchange-striction instead of magneto-striction for the lattice distortion at the transition temperature ?

Réponse de M. Cohen :

The interionic magnetic coupling is predominantly due to exchange via the conduction electron polarization. But we would expect the deformation to result from the total magnetic interaction not just the exchange part.

3. *Intervention de M. Datta :*

In your introduction, you mentionned that in 15 minutes on the basis of Mössbauer spectra, you can distinguish the valence state of Eu (Eu^{2+} or Eu^{3+}). As luminescent chemists, we can say it in 3 seconds. However, I would like to have your comments on the usability of Mössbauer effects in the quantitative analysis of Eu^{2+} and Eu^{3+} when present in the same matrix.

Réponse de M. Cohen :

You can easily do such determinations to a *precision* of a few percent. The *absolute accuracy*, however, is subject to the restriction that the strength (recoil-free-fraction) of the Mössbauer resonance may be different for the two sites, and this can introduce deviations of perhaps 20-30 % in such determinations.

Commentaire de M. Teaney :

The usual magnetic measurements in uniform field are not applicable because Eu is not a simple ferromagnet so that the limit as $H \rightarrow 0$ is not relevant. No transition exists for a simple ferromagnet when $H \neq 0$.

Commentaire de M. Taylor :

Magnetization measurements (at $Q \neq 0$) might be possible using neutrons.

Réponse de M. Teaney au commentaire de M. Taylor :

They might be possible but they are not very probable.