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First-Order Phase Transition in Europium Metal

R. L. COHEN, S. HÜFNER,* AND K. W. WEST
Bell Telephone Laboratories, Murray Hill, New Jersey 07974
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We have used Mössbauer-effect measurements of the hyperfine (hf) interaction in Eu metal to study the behavior of its sublattice magnetization in the vicinity of the magnetic ordering temperature. At 88.6°K, the hf field falls from 0.4 of the saturation value to zero. This results from the existence of a first-order transition coincident with the magnetic ordering. The possible causes of the transition are discussed. The temperature dependence of the hyperfine field just below the transition is analyzed in terms of critical-point theory. The results of thermal-expansion measurements are also presented and discussed.

I. INTRODUCTION

THERE has been a renewed interest in the behavior of substances in the vicinity of critical points of their phase diagrams[1] ever since the derivation of the "scaling laws." In particular, many investigations of magnetic systems in the vicinity of the ordering temperature have been performed, though there are a number of difficulties connected with the extraction of the relevant parameters from the experimental data. In particular, the temperature dependence of the sublattice magnetization has been measured for a number of compounds in the vicinity of the critical temperature. With this aim in mind, a measurement of the temperature dependence of the hyperfine (hf) fields in Eu metal was undertaken.[2] As a result of these measurements, we found that the paramagnetic to antiferromagnetic transition in Eu metal is of first order. This article mainly presents the experimental evidence of this and discusses the causes for the first-order transition, and only secondarily will we discuss the result in terms of a crtical-point analysis. For clarity, we have chosen to call the temperature at which the hf field disappears T_t ($=88.6\pm0.3$°K) in our sample. The term T_N represents the temperature at which the hf field, extrapolated on the basis of a power law from points just below T_t, would go to zero if the first-order transition did not take place. T_N is about 1°K above T_t.

In addition to the Mössbauer measurements, a thermal-expansion measurement was performed in order to check whether there was any anomalous change of the lattice parameters at the magnetic ordering temperature.

There are two previous measurements on the Mössbauer effect in Eu metal.[3,4] These experiments did not observe the sharp transition reported here, probably because of inadequate sample purity.

II. PROPERTIES OF Eu METAL

Eu is divalent in Eu metal, which has bcc structure. This can be inferred from the isomer shift observed in

* Present address: Freie Universität Berlin, Berlin, West Germany.

[1] Recent work has been surveyed in two extensive reviews: L. P. Kadanoff *et al.*, Rev. Mod. Phys. **39**, 395 (1967); P. Heller, Rept. Prog. Phys. **30**, 731 (1967).

[2] Preliminary results were reported in S. Hüfner, R. L. Cohen, and K. W. West, Bull. Am. Phys. Soc. **13**, 876 (1968). The present measurements were performed on samples of greater purity than the rolled metal foils used earlier.

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

[4] P. Kienle, Rev. Mod. Phys. **36**, 372 (1963).

Mössbauer measurements, specific heat,[5] magnetization,[6,7] and neutron diffraction[8] measurements as well as from the different atomic volume as compared to the neighboring rare-earth metals in the periodic table. It should be particularly stressed that the Mössbauer measurements give no indication that even a small fraction of the Eu ions is in a trivalent state. Therefore, the Eu ions have a $^8S_{7/2}$ ground state. The first excited state of the $4f^7$ configuration is $^6P_{7/2}$ at about 25 000 cm^{-1}, and, therefore, it lies far above the ground state. The magnetic structure of Eu has been determined from neutron diffraction[8] experiments as being "flat spiral." The Eu-ion moments, with a value of (5.9 ± 0.4) μ_B, lie in layers in the cube faces (all the moments in one face plane being parallel) with a turn angle of about 50° between the moments in adjacent layers; this turn angle is constant from $T=0$°K up to about $T=0.8T_t$ and then increases slightly to 53° close to T_t. The temperature of the magnetic transition has been found to lie near 90°K.[3–6,8] Additionally, magnetization measurements[7] have revealed a large magnetic anisotropy because in fields as high as 140 kOe, saturation could not be obtained. The exchange has been shown recently to be of relatively long range.[9] Band-structure calculations[10] have shown that the d bands lie very near to the Fermi surface and, therefore, the electronic properties of Eu metal should reflect the d character of the conduction bands.

The hf field H in Eu comes primarily from core polarization due to the $4f$ electrons and from conduction electron polarization.[9] Since both these terms are proportional to sublattice magnetization, H should also be. However, because the magnetic spiral angle changes with temperature, the contribution of the conduction electron polarization to the hf field is not exactly proportional to the $4f$ moment. This effect is unimportant in this work.

III. MÖSSBAUER-EFFECT MEASUREMENTS

A. Experimental Technique

The hf interaction was studied using the Mössbauer effect in transmission geometry with a standard constant-acceleration spectrometer.[11] The source was Sm_2O_3 containing Sm^{151}, which undergoes β decay to the 21.7-keV state in Eu^{151}. The source was held at about 78°K during the experiments. All isomer shifts quoted are relative to an absorber of Eu_2O_3 at 78°K.

The absorber was made by evaporating, in an ultrahigh vacuum system, commercially supplied "triple-distilled" Eu metal onto an outgassed beryllium disc. The Eu layer, about 50 mg/cm² thick, was then covered with a layer of evaporated aluminum before being removed from the vacuum. This effectively prevented oxidation of the Eu during transfer between the evaporator and the measuring crysotat. Three absorbers were made, sequentially, during a single evaporation and they appeared to have identical Mössbauer spectra.

The hf spectra (see Figs. 1 and 2) showed no sign of any precipitated impurity, such as Eu_2O_3, EuO, or

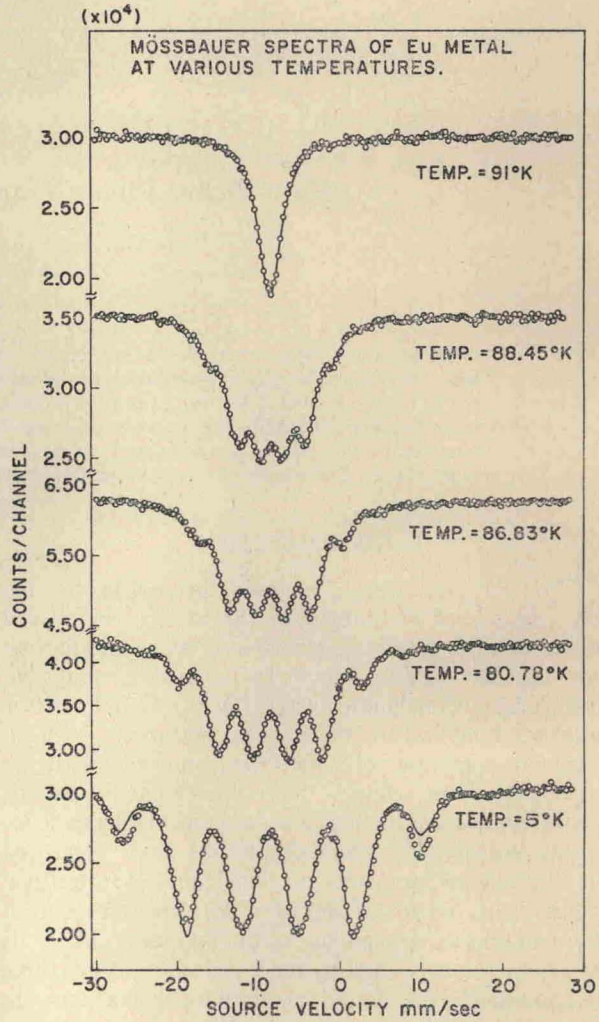

FIG. 1. Spectra of Eu metal above and below T_t. The hfs below the ordering temperature is directly displayed and is proportional to the observed splitting. Each spectrum consists of 18 lines, not all of which are resolved. The solid line is the best fit to the observed points, using line positions and 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.

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