temperature control was free of any overshoot which might have promoted equilibration.

IV. THERMAL-EXPANSION MEASUREMENTS

The differential thermal expansion of a bulk polycrystalline sample of Eu was studied using a standard three-terminal capacitance technique.[13] The sample was taken from the same block used to provide the Eu for making the evaporated absorbers for the Mössbauer experiments. The width and temperature (about 2° lower than T_t measured for the samples made by distillation) of the anomalous thermal-expansion region, shown in Fig. 6, suggest that the nominally "99.9% pure" material contained substantial impurities; this was confirmed by chemical analysis. These impurity problems, plus the polycrystalline nature of the sample, make an exact quantitative analysis of the data impossible, but we can use the measurements to make certain estimates. Of the $\Delta L/L$ change shown in Fig. 6, we consider that about 70 ppm can be attributed to the first-order part of the transition. This corresponds to a volume change of 210 ppm if we assume that the length change of the polycrystalline sample represents a reasonable average of the lattice constant changes so that $\Delta V/V=3\Delta L/L$. The remaining 50 ppm of the $\Delta L/L$ change, presumably, results from the magnetostriction due to the increase of magnetization between the transition temperature and 80°K.

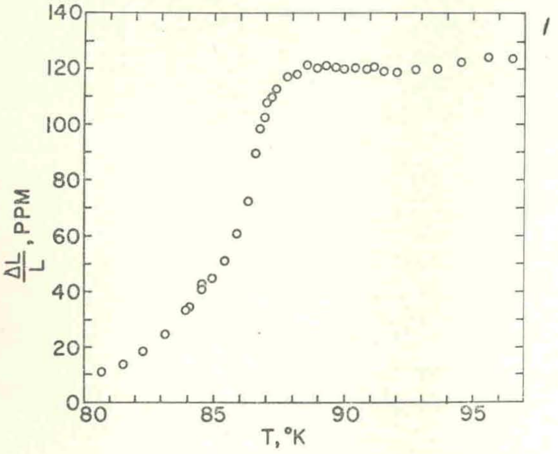

FIG. 6. Differential expansion in the vicinity of T_t for a piece of bulk, polycrystalline Eu metal about 3×3×20 mm long. A constant slope of 20 ppm/°K representing the sample cell expansion plus the normal Eu thermal expansion has been subtracted to emphasize the anomaly.

V. DISCUSSION

A. First-Order Transition

From Fig. 3, it can be seen that at about 88.6°K the hf field suddenly drops to zero from 40% of its saturation value. This discontinuity is characteristic of a first-order phase transition. To our knowledge, this is the first time that it has been suggested that the antiferromagnetic-to-paramagnetic phase transition in Eu metal is of first order. The findings of our experiments are substantiated by very recent specific-heat measurements,[5] which reveal a very sharp peak, in just this temperature regime (see Fig. 7). The total latent entropy of the transition observed by Gerstein *et al.* in this work was 2.7 J/g-at. deg. Assuming that the sublattice magnetization is proportional to the hf field and goes from 40% of saturation to zero, one calculates a magnetic entropy change (using $S=\frac{7}{2}$ and the results of Ref. 14) of 1.7 J/g-at. deg. This indicates a lattice entropy change of about 1 J/g-at. deg. It should be emphasized that the specific-heat measurements, in agreement with our results, showed no hysteresis. Two aspects of the observed first-order transition have to be emphasized: First, to date, no change of the lattice constants of Eu metal has been detected with x-rays in the vicinity of the transition.[15] This is consistent with the results of the thermal-expansion measurements described above; because the x-ray measurements usually only detect changes in the lattice constant down to $\Delta L/L=10^{-4}$, they could not find the small change taking place in Eu metal which we measured by the thermal-expansion technique. Second, the constancy of the isomer shift (*IS*), in going through the critical temperature, shows that there is no change in valence connected with the first-order transition. Note

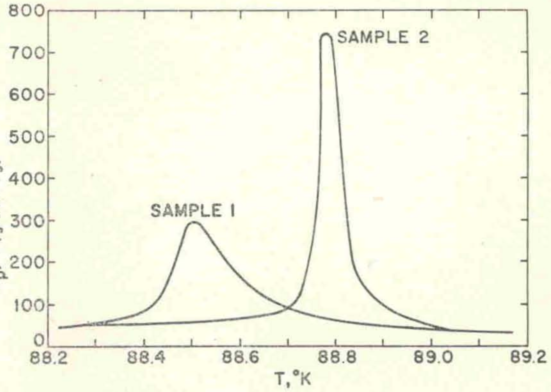

FIG. 7. Curves showing approximate behavior of the specific heat of two samples of Eu, taken from data reported by Gerstein *et al.*, Ref. 5. It is clearly seen that the width and the position of the specific-heat peak at T_t depends strongly on the quality of the sample (sample II was the purer of the two). The sharpness of the peak in sample II is also a strong indication for the first-order transition.

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that though the *IS* values above and below the transition region are the same (see Figs. 3 and 5), there is a small but significant difference between *IS* values for the split and unsplit spectrum components in the transition region.[16]

There are a number of mechanisms that have been discussed recently that can cause a magnetic transition from the paramagnetic to the magnetically ordered state to be of first order. The models, which have been proposed to explain these transitions, all assume that the free energy of the system under consideration contains another term besides those originating from the usual bilinear exchange Hamiltonian.[17] Additional terms arising from the ground-state energy-level scheme[18] ("Blume mechanism"), quadrupole-quadrupole coupling,[19] or magnetostrictive effects[14,20,21] have been discussed. Of these mechanisms, the "Blume mechanism,"[18] the quadrupole-quadrupole coupling,[19] and the cooperative spin-lattice coupling[22] can be ruled out immediately in the present case because of the $^8S_{7/2}$ (spin only) ground state of the Eu ions in Eu metal.

The large observed anisotropy fields[7] suggest a large crystalline anisotropy and, therefore, seem to be at variance with the previous statement. Yet, it has been shown that spiral magnetic structures can result from isotropic-exchange interactions if the exchange integrals, between ions in the *nn* planes and the *nnn* planes, have certain ratios[23,24]; these structures can require high applied fields (comparable to or larger than the exchange) to reach magnetic saturation, as is actually observed in the present case. It has been shown for Eu[9] that exchange interactions extend over large distances, so that coupling to *nnn* planes (and beyond) should be important.

Therefore, we have to assume that either biquadratic exchange[25] or a strong dependence of the net exchange on the lattice parameters[14,20,21] must be responsible for the first-order transition in Eu metal. We are inclined to believe that the second is actually the case—for reasons which will be outlined now. In the simple approach outlined by Herpin *et al.*[23] to explain the development of a spiral structure without any crystalline anisotropy, the turn angle α of the spiral is essentially given by the ratio J_1/J_2, where J_1 and J_2 are the exchange integrals to the *nn* and *nnn* layers, respectively. (The extension to cases where exchange to more distant planes must be considered is obvious.) Since the neutron-diffraction results show that the turn angle changes in approaching the critical temperature, it has to be assumed that the relative magnitudes of the exchange integrals change, i.e., there is a temperature-dependent exchange integral. This is the mechanism used by Bean and Rodbell[14] and also by Lines and Jones.[21] These two treatments are roughly parallel, except that the first considers isotropic lattice changes and the second, distortions from ideal symmetry.

The variation of the Eu ordering temperature and lattice constant with pressure have been obtained by Grazhdankina and McWhan *et al.*[26] These data are adequate to calculate, using the theory of Bean and Rodbell,[14] the "criticality parameter" (proportional to the compressibility times the square of the volume derivative of the transition temperature) for the transition; this value is far too small to produce a first-order transition in the (isotropic) model they consider. The small value of $\Delta V/V$ (≈ 200 ppm), determined from our thermal-expansion results, provides further confirmation of this conclusion. We, therefore, consider a distortion of the lattice with temperature to be the likeliest cause of the change of the exchange interaction with temperature. This is a situation very similar to that observed in MnO and interpreted by Lines and Jones.[21] In Eu, however, the situation is particularly complex in that, because the distortion is caused by the (helical) magnetization, the distortion itself should be a helix in the lattice.

It should be pointed out, in addition, that it is very unlikely that a crystalline anisotropy is responsible for the change in turn angle with temperature, though this is the case with other rare-earth metals. Eu^{2+}, being in a $^8S_{7/2}$ ground-state configuration, has only a very small orbital contribution to its ground-state wave functions induced by higher-order mechanisms. It has also been found that the anisotropy field in EuO, which is a cubic ferromagnet with a Curie temperature of 69°K, has a magnitude of only a few hundred oersteds[27]; this again reflects the lack of orbital contributions to the ground-state wave functions of the Eu^{2+} ions.

It might be argued that the sudden vanishing of the

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[16] The likeliest cause for this would seem to be that a dissolved impurity that changes T_t also changes the *IS*. Thus, part of the absorber having a large impurity concentration (and therefore, e.g., a low T_t) would have a different *IS* from that of a purer absorber segment. Well above and below T_t (since the *IS* difference is very much smaller than the 3-mm/sec linewidth), an "average" *IS* is observed. In the transition region, however, the difference in splittings allows discrimination of "high-T_t" and "low-T_t" material with detection of the different isomer shifts. This analysis supports the view that inhomogeneous dissolved impurities, rather than strain, are the principal source of the transition broadening.

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