We report here the results of magnetic susceptibility, electrical-resistivity, magnetoresistance (MR), heat-capacity and $^{151}$Eu Mössbauer effect measurements on the compound, Eu$_2$CuSi$_3$, crystallizing in an AlB$_2$-derived hexagonal structure. The results establish that Eu ions are divalent, undergoing long-range ferromagnetic-ordering below ($T_C =$) 37 K. An interesting observation is that the sign of MR is negative even at temperatures close to $3T_C$, with increasing magnitude with decreasing temperature exhibiting a peak at $T_C$. This observation, being made for a Cu containing magnetic rare-earth compound for the first time, is of relevance to the field of colossal magnetoresistance.

Large negative magnetoresistance (LNMR) in perovskite-based manganites [colossal magnetoresistance (CMR) systems] peaking in the vicinity of Curie temperature ($T_C$) is one of the most important observations in modern condensed matter physics. In this regard, the observation of negative magnetoresistance, the magnitude of which increases with decreasing temperature peaking near the magnetic ordering temperature temperatures ($T_o$) in the indirect-exchange controlled (not only in ferromagnetic, but also in antiferromagnetic) magnetic systems like those of Gd, Tb and Dy based alloys (by us) calls for mechanisms other than double-exchange and Jahn-Teller effects to explain such features. We have proposed the need to consider the possible role of magnetic polaronic effects even in metallic alloys. The importance of such an observation and hypothesis is apparent also from similar recent reports, both theoretical and experimental, from other groups as well. Apparently, it is not always necessary to observe such features in every Gd alloy and in fact many such alloys show normally expected negligibly small positive magnetoresistance (MR) at all temperatures above $T_o$. However, it was noted that such features, if observed, are restricted to Pd, Pt, Co, Ni or Mn containing compounds, but not to Cu, Ag and Au containing ones, which raise a question whether such anomalies result from the intrinsic tendency of the d bands of the former class of elements to get easily polarised by the 4f local moment. In this article, among other magnetic properties, we emphasize on the observation of LNMR in a (Eu-based) Cu containing alloy for the first time over a wide range of temperature above Curie temperature ($T_C$: Cu being non-magnetic, this result endorses our view that LNMR is a magnetic precursor effect of 4f-ion long-range magnetic ordering.

The investigation of Eu$_2$CuSi$_3$, crystallizing in an AlB$_2$-type hexagonal structure has been undertaken considering current interest in synthesizing and investigating magnetic properties of ternary rare-earth/actinide compounds with the atomic ratios of 2:1:3, particularly those adopting variants of either the tetragonal ThSi$_2$ or hexagonal AlB$_2$ structure types. It is to be noted that the reports on Eu compounds of this type are generally rare. Recently, we reported the synthesis and interesting magnetic behavior of the compound, Eu$_2$PdSi$_3$ [Ref. 19]. The scarcity of the reports on such Eu compounds is presumably due to the difficulties in controlling the Eu stoichiometry during sample preparation. We have carried out electrical resistivity ($\rho$), MR, magnetization (M) and magnetic susceptibility ($\chi$), heat-capacity (C) and $^{151}$Eu Mössbauer effect (ME) studies on Eu$_2$CuSi$_3$, in order to understand the magnetic behavior of this alloy, the results of which are reported here.

The sample was prepared by induction melting stoichiometric amounts of constituent elements in an inert atmosphere. The ingot was melted four times and the loss due to evaporation of Eu after first melting was compensated by adding corresponding amounts of Eu. We noticed negligible loss of Eu in subsequent meltings. The ingot was homogenised in an evacuated, sealed quartz tube at 800°C. X-ray diffraction pattern,
obtained by employing Cu Kα radiation, established that the present compound crystallizes in an AlB2-derived hexagonal structure. Since we do not see any superstructure lines in the x-ray diffraction pattern, we presently believe that there is an intrinsic disorder between Cu and Si sites, unlike Eu2PdSi3 (Ref. 19), and the lattice constants obtained are a= 4.095Å and c=4.488Å. No additional lines attributable to any other phase within the detection limit of x-ray diffraction could be seen.

The ρ measurements (2-300 K) were performed by a conventional four-probe method employing silver paint for making electrical contacts. The sample is found to be very porous and tends to become powder with ageing and hence there are difficulties at arriving absolute values of ρ. The χ measurements (2-300 K) were performed employing a commercial SQUID magnetometer in the presence of several magnetic fields. The C data (2-70 K) were obtained by a semi-adiabatic heat-pulse method. The (longitudinal mode) MR data were obtained in the presence of a magnetic field (H) of 30 kOe in the temperature range 4.2-100 K and also as a function of H at selected temperatures (4.2, 25 and 50 K). 151Eu ME measurements at selected temperatures (4.2 -300 K) were performed employing 151SmF3 source (21.6 keV transition) in the transmission geometry.

The results of ρ (normalised to the value at 300 K), inverse χ (measured in the presence of 2 kOe) and C measurements are shown in Fig. 1, only below 100 K; the data at higher temperatures are not shown as there are no interesting features to be highlighted. It is clear that there is a sudden drop in ρ at 37(1) K as the temperature is lowered. This drop arises from the onset of magnetic ordering as evidenced below. There is a distinct anomaly even in the temperature dependent C data around 37 K, which originates from magnetic ordering. The χ is found to exhibit Curie-Weiss behaviour in the temperature range 40-300 K and the effective moment obtained from this linear region is found to be 7.8 µB/Eu, which is very close to that expected for divalent Eu ions, thereby confirming that all the Eu ions are divalent in this compound. This also suggests that there is no magnetic moment on Cu. The value of the paramagnetic Curie-temperature (θp) is found to be 38 K; inverse χ tends to saturate below the same temperature. These results establish that Eu ions undergo a ferromagnetic-type of magnetic ordering at 37(1) K; this temperature is practically the same as θp, indicating absence of competition from antiferromagnetic interaction, a situation different from that observed for Eu2PdSi3 (Ref. 19).

There are also qualitative changes in the low temperature susceptibility behavior measured at different fields, as seen in Fig. 2. In addition to the sharp rise of χ around 40 K due to the onset of ferromagnetic ordering, there is a peak at about 5 K followed by a drop at lower temperatures for the data recorded in the presence of 100 or 1000 Oe, a feature absent (but showing a weak upturn) for the application of a higher field (say, 2 kOe). This might imply the presence of another magnetic transition around 5 K, which is modified with increasing magnetic field. This may be corroborated to the observation of a very weak peak in C around 5 K (visible if the plot of the low temperature data is drawn in an expanded scale). Presumably, the two magnetic transitions arise from two types of Eu ions with different chemical environment, which may be intrinsic to these 2-1-3 class of alloys. Possibly the degree of Cu-Si disorder is actually small. The evidence for two types of Eu ions can be found even in the Mössbauer data and the broadening of the spectra of the minority site due to the transferred hyperfine field from the majority site (discussed below) establishes that minority Eu is not extrinsic to the sample. We also note that the zero-field and field-cooled data diverge at Tc as the temperature is lowered, presumably due to anisotropy of the material; this divergence can not arise from spin-glass phenomenon, considering that the features in C and ρ are sharp at the magnetic transition. We may also add that there is a hysteretic behavior of the isothermal M with a small coercive field (300 Oe) at 2 K, but with a still smaller value of coercive field at 10 K, if measured as a function of H (Fig. 3), typical of soft ferromagnets. It is obvious from Fig. 3 that the isothermal M does not saturate even at high fields and the value, say at 2 K for H= 50 kOe is far below the full value of 14µB/formula unit; which may suggest that the ferromagnetism could be of a canted-type.

We have also performed 151Eu Mössbauer effect measurements as a function of temperature in order to get a microscopic picture of the magnetism. It may be re-
marked that the $^{151}$Eu ME studies at 300 K for the composition, EuCu$_{0.5}$Si$_{1.5}$, was reported in Ref. 24 several years ago, as a continuation of substitutional studies in EuSi$_2$, but to our knowledge there has been no further study on this alloy. Typical spectra obtained at various temperatures are shown in Fig. 4, reflecting the magnetic behavior below 38 K. The spectrum at 38 K indicates the absence of magnetic order at this temperature, with the dominant feature at -10.5 mm/s characteristic of divalent Eu ions. A weak feature around zero velocity (at -0.2 mm/s) with about 3% fractional intensity (as derived from the low temperature spectra) arises from trivalent Eu ions, presumably produced by surface oxidation when powdering the sample for the preparation of the absorber. The magnetic hyperfine split spectra below 38 K could not be consistently fitted with only one site; the assumption of two sites with the same intensity ratio of 3:1 as in Eu$_2$PdSi$_3$ (Ref. 19), however, resulted in a better description of the observed data. The isomer shifts of the two sites are almost identical (-10.4 and -10.7 mm/s), in contrast to distinctly different values (-10.0 and -8.6 mm/s) observed in Eu$_2$PdSi$_3$. The hyperfine fields, $B_{\text{eff}}$, of the two sites exhibit, similar to the Eu$_2$PdSi$_3$ case, a drastically different temperature dependence, as displayed in Fig. 5. At 4.2 K, the values of $B_{\text{eff}}$, -290 and -315 kOe, are rather close for the majority and minority sites, unlike the situation in Eu$_2$PdSi$_3$ (in which case the corresponding values are -408 and -255 kOe respectively). Since the unit-cell volumes of these Cu and Pd containing alloys are almost identical, the differences in isomer shifts and hyperfine fields between these two compounds may be attributed to different transition metal ion surrounding for Eu. Obviously, the influence of Pd is stronger in bringing about a local modification of the conduction electron characteristics around the two Eu sites. In addition, Pd and Cu environments also modify the nature of magnetic ordering; while in the Pd case there is an evidence for antiferromagnetic coupling, the magnetic ordering is of a ferromagnetic type in the Cu case. It should also be noted that the plot of $B_{\text{eff}}$ versus temperature does not follow the magnetization curve expected for a $S=7/2$ spin system, which may be indicative of some degree of crystallographic disorder. There is a transfer of hyperfine field to the minority Eu site below 38 K as indicated by the broadening of the spectral features of this site, however, with the minority site ordering magnetically only at lower temperatures. Around 6 K, similar to a feature in the $\chi$ data, there is a noticeable change in the $B_{\text{eff}}(T)$ curves for both the sites, indicating a rearrangement of the spin direction, possibly resulting in a canted ferromagnetic alignment. From the absence of a significant reduction in the value of $B_{\text{eff}}$ below that due to core-polarization contribution, following the arguments given in our earlier article, we conclude that the antiferromagnetic coupling is however negligible. This is consistent with the observation that, besides the sign, the magnitude of $\theta_p$ is the same as $T_C$.

We now present an observation of importance to the field of CMR. An application of H (say, 30 kOe) depresses the value of the electrical resistance, resulting in a negative MR even around 100 K, which is far above $T_C$ (Fig. 6). The magnitude of MR, defined as $\Delta \rho/\rho = (\rho(H)-\rho(0))/\rho(0)$, grows with decreasing temperature peaking at $T_C$, as shown in Fig. 6, similar to the behavior observed in by now well-known perovskites-based La manganites (CMR systems). Needless to mention that the negative MR in the ferromagnetically ordered state is usually expected. The data were also collected (Fig. 6, bottom) as a function of H at selected temperatures both above and below $T_C$ in order to correlate the values with those obtained from the temperature dependent measurements. It is clear that the value is as large as about -9% at 70 kOe even at 50 K. We also remark that there is a sign crossover around 120 K, beyond which one sees a positive MR; for instance, in a field of 30 kOe at 200 K, the value is about 2%, which reduces to negligibly small (but positive) values at 300 K (not shown in the figure).

To conclude, the compound, Eu$_2$CuSi$_3$, crystallizing in a AlB$_2$-derived hexagonal structure, exhibits long-range ferromagnetic ordering at 37 K. The temperature dependent magnetoresistance behavior is qualitatively similar to that observed in CMR systems, though double-exchange or Jahn-Teller mechanisms are not operative in such Eu systems. Similar temperature dependent behavior in the paramagnetic state has been made by us in the past in some Gd, Tb, Dy based alloys. The uniqueness of the present result is that such an observation is made for the first time in a Eu-based / Cu-based alloy. The Cu
ions do not carry any magnetic moment and therefore the present results establish that the observed magnetoresistance anomalies in the vicinity of magnetic transition temperature is solely related to magnetic precursor effect due to 4f magnetism. We suggest that the alloys exhibiting such features should be viewed together with LNMR systems to understand this phenomenon better. The results also give a clue to identify potential candidates exhibiting large MR at room temperature for applications in the sense that one can search for magnetic precursor effects in compounds undergoing magnetic ordering at temperatures rather close to (but below) 300 K.

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FIG. 1. Inverse susceptibility, electrical resistivity normalised to the value at 300 K ($\rho(T)/\rho(300K)$), and heat-capacity in the temperature range 2 - 100 K for Eu$_2$CuSi$_3$.

FIG. 2. Magnetic susceptibility below 70 K measured in the presence of various fields for Eu$_2$CuSi$_3$. All the data were recorded in the zero-field cooled (ZFC) state of the specimen. For H= 100 Oe only, the data in field-cooled (FC) state are also shown. Continuous lines are drawn through the data points for H= 100 Oe.

FIG. 3. Magnetic hysteresis curves at 2 and 10 K for Eu$_2$CuSi$_3$. The low field data is shown in an expanded form in the insets. The lines drawn through the data points are guides to the eyes.

FIG. 4. $^{151}$Eu Mössbauer spectra at various temperatures for Eu$_2$CuSi$_3$. The continuous lines through the data points represent least-square fits of the data. The subspectra for T < 38 K are also shown.

FIG. 5. The magnitude of the magnetic hyperfine fields plotted as a function of temperature, obtained from the data shown in Fig. 4 for divalent Eu ions with two different crystallographic environments. Filled circles are for majority Eu ions and the open circles are for minority Eu ions. The lines through the data points are guides to the eyes. The sign of $B_{eff}$ is negative.

FIG. 6. Electrical resistivity normalised to 300 K value as a function of temperature for Eu$_2$CuSi$_3$ in zero field as well as in 30 kOe. The magnetoresistance values derived from this data are also shown in this figure. The magnetoresistance as a function of field at selected temperatures is shown in the lowest part of the figure. The lines drawn through the data points serve as guides to the eyes.
