The superconducting compound Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ and the normal conducting compound Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ were studied by $^{151}$Eu and $^{57}$Fe Mössbauer spectroscopy (MS) and magnetometry at temperatures ranging from 5 to 297 K. The $^{151}$Eu MS studies showed that in both compounds, the europium magnetic moments order helically (at $T_M = 18$ and 20 K, respectively) with a tilting angle of about 36° to the c-axis, whereas in pure EuFe$_2$As$_2$ where the Fe is magnetically ordered, they order perpendicular to the c-axis. We concluded that this change is due to the disappearance of iron magnetism in the mixed compounds. Although the iron ions are nonmagnetic in both the superconducting and the normal conducting compound, $^{57}$Fe MS studies display, at 5 K, magnetic hyperfine structure due to transferred magnetic hyperfine fields (∼1 T) from the magnetically ordered Eu sublattice.
1. Introduction

Over the last few years, much progress has been made in establishing superconductivity unambiguously in MFe$_2$As$_2$ (also known as 122, M = Ba, Sr, Ca and Eu) systems [1]–[6]. The pristine MFe$_2$As$_2$ sample that has a spin-density-wave (SDW) ground state is pushed in the M(Fe$_{1-x}$T$_x$)$_2$As$_2$ (T = Co, Ni, etc) systems to a superconducting (SC) state by electron/hole doping and the application of pressure [7]–[12]. It is also well established that superconductivity emerges when the SDW state is suppressed. Band-structure calculations point out that the SDW state arises on account of the special two-dimensional (2D) geometry of the Fermi surface that is unstable to nesting. Also associated with or preceding the magnetic transition is a tetragonal-to-orthorhombic structural transition, which is suppressed in the SC state [13, 14].

The strong interplay among structure, magnetism and electronic structure has been investigated recently for the substituted Eu(Fe$_{1-x}$T$_x$)$_2$As$_2$ (T = Co, Ni) systems, in which Eu$^{2+}$ ions carry local magnetic moments and order magnetically around 20 K. The well-established phase diagrams indicate that in Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ [15], (i) the Fe ions are not magnetically ordered, (ii) the sample is not SC and (iii) the Eu ions are ferromagnetically (FM) ordered at $T_M = 20$ K. On the other hand, Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ is SC below $T_C = 21$ K; below $T_M = 17$ K, a complicated helical magnetic structure for the Eu$^{2+}$ spins is proposed [16]. Thus, at low temperatures, superconductivity in the Fe-As layers and the Eu ordered magnetic state coexist.

After the discovery of Mössbauer spectroscopy (MS) half a century ago, superconductivity was one of the subjects, among many others, that this method was able to investigate. Mössbauer probes in conventional superconductors yield relatively little information. However, in the new magneto-SC systems Eu(Fe$_{1-x}$T$_x$)$_2$As$_2$, $^{57}$Fe MS may contribute much, since the Fe ions are not probes but rather part of the layers to which superconductivity is confined. By using the two, $^{57}$Fe and $^{151}$Eu, isotopes, MS is a useful tool for investigating simultaneously the mutual interaction between the magnetic Eu and the Fe layers, regardless of whether the Fe-As layers are SC or not. MS can also determine the Eu sublattice moments’ direction and its effect on the SC state.

In our previous publications, we have shown that the effective magnetic hyperfine field ($H_{eff}$) direction of Eu$^{2+}$ is strongly affected by the magnetic ground state of the Fe sublattice. For materials in which the Fe ions are in the SDW ground state (such as EuFe$_2$As$_2$), the Fe magnetic anisotropy pulls the Eu magnetic moment direction, and that of $H_{eff}$, to be parallel to the $ab$-plane. On the other hand, in the absence of Fe magnetism, like in SC materials or in EuFe$_2$P$_2$ where the SDW magnetic state of iron is totally suppressed, the direction of $H_{eff}$ is parallel to the $c$-axis [17]–[19].

For understanding such an interplay more deeply, we measured the MS spectra of the two, $^{57}$Fe and $^{151}$Eu, isotopes, in Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ and Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ samples, in which the doping concentration is almost the same. The first material is SC but the latter one is not SC down to 2 K. We show that the MS spectra of the two samples are practically the same, confirming our determination stated above that only the Fe magnetic state affects the ordered Eu sublattice direction.

2. Experimental details

The polycrystalline Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ sample and the single crystal of Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ were prepared and characterized as described in detail in [15] and [16], respectively. Zero-field-cooled (ZFC) and field-cooled (FC) temperature dependence dc magnetization measurements
Figure 1. ZFC and FC magnetization branches for Eu(Fe_{0.89}Co_{0.11})_{2}As_{2} measured at 3 Oe when $H \parallel ab$. The subtraction of the two curves is shown in the inset.

at various applied fields were carried out in a commercial MPMS5 Quantum Design SQUID magnetometer. Mössbauer studies on powder samples were performed using a conventional constant acceleration drive. The sources were 50 mCi $^{57}$Co : Rh for the $^{57}$Fe spectra and 100 mCi $^{151}$Sm_{2}O_{3} for the $^{151}$Eu spectra. The absorbers were cooled down to 5 K, in a Janis model SHI-850-5 closed cycle refrigerator. The spectra were analyzed using least squares fit procedures to theoretically expected spectra, including full diagonalization of the hyperfine interaction spin Hamiltonian. The analysis of $^{151}$Eu spectra considered also the exact shape of the source emission line [19]. Velocity calibration was performed with an $\alpha$-iron foil at room temperature. The reported isomer shift (IS) values for Fe or Eu are relative to the Fe foil or Eu_{2}O_{3} at room temperature.

3. Experimental results

3.1. (a) Magnetic and Mössbauer spectroscopy (MS) studies in Eu(Fe_{0.89}Co_{0.11})_{2}As_{2}

The SC features (below $T_{C} \sim 21$ K) that are confined to the Fe–As layers, and the magnetic structure of the Eu$^{2+}$ sublattice (below $T_{M} = 17$ K) for Eu(Fe_{0.89}Co_{0.11})_{2}As_{2}, as well as its crystal structure and lattice parameters, have already been discussed intensively in [16]. In order to check the quality of the crystal on which the MS studies have been performed, we have repeated a few magnetic measurements, which are exhibited in figures 1–3. Due to the proximity of $T_{C}$ and $T_{M}$, the high magnetic moment of the Eu$^{3+}$ ions masks the SC diamagnetic signals and the SC state was detected by resistivity studies only [16].

Figure 1 shows the ZFC and FC branches for Eu(Fe_{0.89}Co_{0.11})_{2}As_{2} measured at 3 Oe when the applied field ($H$) is parallel to the $ab$-plane. The subtraction of the FC–ZFC curves is shown in the inset. The distinct peak at 17 K in both curves indicates an antiferromagnetic (AFM) type ordering of the Eu sublattice. Due to the presence of a small amount of Eu$^{3+}$ as a foreign phase (see figure 4), the two curves merge at $T_{C} = 25.5 \pm 0.5$ K, which is $\sim 4$ K higher than
Figure 2. ZFC and FC magnetization branches for \( \text{Eu(Fe}_{0.89}\text{Co}_{0.11})_{2}\text{As}_2 \) measured at 3 Oe when \( H \) is parallel to the \( c \)-axis.

Figure 3. ZFC and FC susceptibility curves of \( \text{Eu(Fe}_{0.89}\text{Co}_{0.11})_{2}\text{As}_2 \) measured at 1 kOe in both the \( H \parallel ab \) and \( H \parallel c \) directions.

\( T_C \) obtained by resistivity measurements [16]. At higher applied fields (say at 100 Oe), the two ZFC and FC branches coincide (see also figure 3). In the ZFC branch, the moment at 5 K is about 2/3 of its value at \( T_M \), similar to what was reported in [16]. Another anomaly is observed around 13 K, which may be attributed to a tiny spin reorientation of the Eu\(^{2+}\) ions. The slight difference between the ZFC and FC branches presumably arises from the AFM alignment of the Eu sublattice. Since the direction of the Eu moment is helically distributed (see below), it is assumed that in the FC process the external field causes the Eu spins to cant slightly out of their original direction. This canting abruptly aligns a component of the moment with the \( H \) direction and the FC is obtained. Alternatively, due to the SC state, this bifurcation may be caused by flux trapping at \( T_C \).
The ZFC and FC branches measured at 3 Oe when $H$ is along the $c$ direction are depicted in figure 2. Below $T_M$, the magnitude of the moments of the two curves remains nearly constant. As stated above, the slight difference between the two curves may be caused by the flux pinning in the SC state.

Figure 3 shows the ZFC/FC plots (which coincide) measured at 1 kOe in both orientations. The different nature of the two curves is quite obvious. The higher susceptibility ($M/H$) values of the $H \parallel ab$ curve (the ratio at $T_M$ is 1.87) indicates that the planes are the preferred easy axis of magnetization, similar to EuFe$_2$As$_2$ as discussed above. The same trend is also observed at low $H$ when one compares the values depicted in figures 1 and 2. The nearly constant values obtained along the $c$ direction also confirm this determination. For an ideal AFM (without taking into account the demagnetization factors), for both orientations, the moment at $T_M$ should be the same. In the present case, the absence of a demagnetization factor along the $c$-axis should increase the moment values in this direction. Therefore, a more complicated structure such as a non-collinear helical alignment for the Eu spins in Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ is proposed in [16].

MS studies of $^{151}$Eu and $^{57}$Fe in Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ at temperatures ranging from 5 to 297 K were performed. The $^{151}$Eu MS spectra below (5.1 K), at (17 K) and above (19 K) the magnetic transition of Eu$^{2+}$ ions are displayed in figure 4. All spectra show the presence of a tiny amount (<4%) of a foreign Eu$^{3+}$ phase. The measured IS values $-12.1(1)$ mm s$^{-1}$ are typical of Eu$^{2+}$ ions. The negative quadrupole interactions ($\frac{1}{2}e^2qQ_0$) range between $-2.5$ and $-2.0$ mm s$^{-1}$. Below the magnetic transition, the $^{151}$Eu spectra display magnetic hyperfine structure, and the saturation magnetic hyperfine field ($H_{sat}$) at 5 and 10 K is 29.4 and 23 T, respectively, in good agreement with values obtained for the SC materials in the EuFe$_2$(As$_{1-x}$P$_x$)$_2$ system [19]. The MS at 17 K is somewhat broader than that at 19 K, which indicates that small magnetic fluctuations still exist at $T_M = 17$ K as deduced from figures 1–3.
Thus, the real magnetic transition is about 18 K. The narrow spectrum at 19 K (figure 4) resembles the MS spectra measured at elevated temperatures up to 295 K.

The interesting observation is the negative quadrupole shift \( \frac{1}{2} Q_0 (3 \cos^2 \theta - 1) / 2 \), where \( \theta \) is the angle between the hyperfine field and the main axis of the electric field gradient, the \( c \)-axis in the present case, obtained below the magnetic transition. Similar negative values have been obtained in EuFe\(_2\)P\(_2\) and in all mixed compounds such as EuFe\(_2\)\((\text{As}_1-x,\text{P}_x)\)\(_2\) in which the SDW magnetic state of Fe is suppressed. On the other hand, a positive quadrupole shift has been obtained in EuFe\(_2\)\(_c\)\(_x\)\(_\text{As}\(_2\)\). Therefore, we may assume that in Eu(Fe\(_{0.89}\)Co\(_{0.11}\))\(_2\)\(_\text{As}\(_2\)\) the \( H_{\text{eff}} \) direction is basically along the \( c \)-axis. Analyzing the MS spectra at 5 K and at 10 K (not shown) with a full diagonalization of the hyperfine spin Hamiltonian yields a better fit with the quadrupole interaction \( \frac{1}{2} Q_0 = -2.35 \text{ mm s}^{-1} \) and \( H_{\text{eff}} \) is tilted away from the \( c \)-axis by \( \sim 36^\circ \), indicating a helical spin structure, as discussed in the previous section. Since Eu(Fe\(_{0.89}\)Co\(_{0.11}\))\(_2\)\(_\text{As}\(_2\)\) is also SC (at \( T_c = 21 \) K), this material serves as another example in which magnetism and superconductivity coexist.

The \(^{57}\text{Fe}\) MS spectra of Eu(Fe\(_{0.89}\)Co\(_{0.11}\))\(_2\)\(_\text{As}\(_2\)\) measured below and above \( T_M \) are displayed in figure 5. The spectrum at room temperature was analyzed in terms of two broad quadrupole doublets, originating from non-equivalent iron ions according to their Co neighbors with IS = 0.46(1) and 0.43(1) mm s\(^{-1}\) and quadrupole splitting QS \( \left( \frac{1}{2} Q_0 \right) = 0.52(1) \) and 0.17(1) mm s\(^{-1}\), respectively. In EuFe\(_2\)\(_\text{As}\(_2\)\), only one small QS \( \sim 0.15 \text{ mm s}^{-1} \) is observed; however, the replacement of Fe by Co or Ni [17] or the replacement of As by P [19] produces the second larger QS site. The spectrum at 5 K displays magnetic hyperfine structure, and was analyzed in terms of two hyperfine fields. At 5 K the \( H_{\text{eff}} \) values obtained are 0.39 and 1.05 T for the two sub-spectra, respectively, values that are quite similar to those obtained in other related systems [18]. Since in the SC Eu(Fe\(_{0.89}\)Co\(_{0.11}\))\(_2\)\(_\text{As}\(_2\)\) compound the Fe ions are diamagnetic, the hyperfine fields observed are transferred fields from the magnetically ordered Eu sublattice as suggested for EuFe\(_2\)\(_\text{As}\(_2\)\) in the past [20]. The best fit to the 5 K experimental spectrum is obtained when the transferred fields point in the same direction as that of the Eu magnetic moment. This is a rare phenomenon that also was observed in a similar SC EuFe\(_2\)(As\(_{0.68}\)P\(_{0.32}\))\(_2\) compound [19]. In systems such as ErRh\(_2\)\(_B_3\) [21], RE\(_5\)Mo\(_6\)S\(_8\) [22], RNi\(_2\)\(_B_2\) [23] or RuR\(_2\)\(_{1-x}\)Ce\(_x\)S\(_2\)Cu\(_2\)O\(_10\) [24] (R = rare-earth) in which coexistence of superconductivity and magnetism is well established, the two states are confined to different site locations.
3.2. (b) MS studies in Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$

The extensive magnetic measurements on Eu(Fe$_{1-x}$Ni$_x$)$_2$As$_2$ up to $x = 0.2$ reveal that Ni suppresses (as expected) the SDW ground state of Fe in EuFe$_2$As$_2$ and that for $x > 0.08$, the Fe ions are diamagnetic [15]. No SC state was found in the entire measured system. Moreover, for $x > 0.03$ the magnetic ordering of Eu$^{2+}$ (about 20 K) changes from AFM to ferromagnetic (FM). Our main goal here is to compare the SC compound Eu(Fe$_{0.89}$Co$_{0.11}$)$_2$As$_2$ and the normal conducting compound Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$; both have practically the same doping concentration. The $^{57}$Fe MS spectra of Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ were shown in our previous publication [17].

Figure 6 shows the MS spectra of Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ and EuFe$_2$As$_2$, both measured at 5 K. The Ni-doped sample exhibits the presence of about 8% of foreign Eu$^{3+}$, which originates from surface oxidation of the Eu$^{2+}$ ions. The IS is $-11.75(2)$ mm s$^{-1}$ and the negative quadrupole interaction is $-2.35$ mm s$^{-1}$. The $H_{\text{eff}}$ obtained is 28.7(2) T and the tilting angle from the $c$-axis is $\sim 34^\circ$. An easy determination of the orientation of $H_{\text{eff}}$ can be obtained by comparing the two spectra exhibited in figure 6. Whereas for EuFe$_2$As$_2$ (where $H_{\text{eff}}$ is along the $c$-axis)

![Figure 6. $^{151}$Eu Mössbauer spectra of Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ and EuFe$_2$As$_2$. Note that the peak intensities increase from left to the center in the latter compound, whereas the opposite trend is observed in the Ni-doped material.](http://www.njp.org/)

New Journal of Physics 13 (2011) 023033 (http://www.njp.org/)
the peak intensity increases from left to the center, the opposite trend is observed for both Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ and Eu(Fe$_{0.85}$Co$_{0.15}$)$_2$As$_2$ (figure 4) samples.

Generally speaking, the hyperfine parameters obtained for Eu, in Eu(Fe$_{0.9}$Ni$_{0.1}$)$_2$As$_2$ and Eu(Fe$_{0.85}$Co$_{0.15}$)$_2$As$_2$, in particular the Eu negative quadrupole interaction and the tilting of $H_{\text{eff}}$ from the $c$-axis, are almost the same. This indicates a similar magnetic structure regardless of whether the system is normal conducting or SC. This observation confirms our previous assumption that in the 122 systems the direction of the Eu$^{2+}$ (S state ion) sublattice magnetic moments is strongly affected by the magnetic behavior of Fe atoms. As a rule, when the Fe ground state is magnetic the direction of the Eu magnetic moment is along the $ab$-plane [25, 26]. The opposite trend is obtained for non-magnetic Fe ground states, in which the Eu magnetic moment is along the $c$-axis.

Acknowledgments

Our research work in Jerusalem was partially supported by the Israel Science Foundation (ISF; Bikura 459/09), by the joint German–Israeli DIP project and by the Klachky Foundation for Superconductivity. Our research work in China was supported by the National Basic Research Program of China (grant no. 10934005) and the Fundamental Research Funds for the Central Universities of China (grant no. 2010QNA3026).

References

[1] Rotter M, Tegel M, Johrendt D, Schellenberg I, Hermes W and Pottgen R 2008 Phys. Rev. B 78 020503R
[2] Rotter M, Tegel M and Johrendt D 2008 Phys. Rev. Lett. 101 107006
[3] Sasmal K, Lv B, Lorenz B, Guioy A M, Chen F, Xue Y Y and Chu C W 2008 Phys. Rev. Lett. 101 107007
[4] Ren Z, Zhu Z, Jiang S, Xu X, Tao Q, Wang C, Feng C, Cao G and Xu Z 2008 Phys. Rev. B 78 052501
[5] Jeevan H S, Hossain Z, Kasinathan D, Rosner H, Geibel C and Gegenwart P 2008 Phys. Rev. B 78 092406
[6] Torikachvili M S, Bud’ko S L, Ni N and Canfield P C 2008 Phys. Rev. Lett. 101 057006
[7] Li L J et al 2009 New J. Phys. 11 025008
[8] Ni N, Bud’ko S L, Kreyszig A, Nandi S, Rustan G E, Goldman A I, Gupta S, Corbett J D, Kracher A and Canfield P C 2008 Phys. Rev. B 78 014507
[9] Sefat A S, Jin R, McGuire M A, Sales B C, Singh D J and Mandrus D 2008 Phys. Rev. Lett. 101 117004
[10] Alireza P L, Ko Y T C, Gillett J, Petrone C M, Cole J M, Lonzarich G G and Sebastian S E 2008 J. Phys.: Condens. Matter 21 012208
[11] Mani A, Ghosh N, Paulraj S, Bharathi A and Sundar C S 2009 Eur. Phys. Lett. 87 17004
[12] Ni N, Thaler A, Yan J Q, Kracher A, Colombier E, Bud’ko S L and Canfield P C 2010 Phys. Rev. B 82 024519
[13] Singh D J 2009 Physica C 469 418
[14] Kasinathan D, Ormeci A, Koch K, Burkhardt U, Schnelle W, Leitner-Jasper A and Rosner H 2009 New J. Phys. 11 025023
[15] Ren Z, Lin X, Tao Q, Jiang S, Zhu Z, Wang C, Cao G and Xu Z 2009 Phys. Rev. B 79 094426
[16] Jiang S, Xing H, Xuan G, Ren Z, Wang C, Xu Z and Cao G 2009 Phys. Rev. B 80 184514
[17] Nowik I and Felner I 2009 Physica C 469 485
[18] Feng C, Ren Z, Xu S, Jiang S, Xu Z, Cao G, Nowik I, Felner I, Matsubayashi K and Uwatoko Y 2010 Phys. Rev. B 82 094426
[19] Nowik I, Felner I, Ren Z, Cao G H and Xu Z A 2011 J. Phys.: Condens. Matter 23 065701
[20] Raffius H, Morsen E, Mosel B D, Muller-Warmuth W, Jeitschko W, Terbuch I and Vomhof T 1993 J. Phys. Chem. Solids 54 135

New Journal of Physics 13 (2011) 023033 (http://www.njp.org/)
[21] Fertig W A, Johnston D C, Delong L E, McCallum R W, McCallum R W, Maple M B and Matthias B T 1977 Phys. Rev. Lett. 38 987
[22] Fischer O, Treyvaud A, Chevrel R and Sergent M 1975 Solid State Commun. 17 721
[23] Yaron U, Gammel P L, Ramirez A P, Huse D A, Bishop D J, Goldman A I, Stassis C, Canfield P C, Mortensen K and Eskildsen M R 1996 Nature 382 236
[24] Felner I, Asaf U, Levi Y and Millo O 1997 Phys. Rev. B 55 R3374
[25] Nowik I and Felner I 1986 Hyperfine Interact. 28 959
[26] Xiao Y et al 2009 Phys. Rev. B 80 174424