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# Phase stability, structure and magnetic properties of $R_3(\text{Fe, TM})_{29}$ , ( $R=\text{Gd, Dy, Er, Y}$ and $\text{TM}=\text{V, Ti}$ ) compounds with disordered structures

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## Abstract

The  $R_3(\text{Fe,V})_{29}$  compounds, with  $R=\text{Dy, Er, Y}$ , and the  $\text{Gd}_3(\text{Fe, TM})_{29}$ , with  $\text{TM}=\text{Ti}$  and  $\text{V}$ , after heat treatment between 1123 and 1233 K form disordered structures that belong in the  $\text{CaCu}_5$  type family. The compounds with  $R=\text{Y}$  or  $\text{Dy}$  and  $\text{TM}=\text{V}$  crystallize in a disorder  $\text{CaCu}_5$  structure type (space group (S.G.):  $P6/mmm$  with cell dimensions  $a=4.8769(1)$  Å,  $c=4.1729(3)$  Å and  $a=4.8692(2)$  Å,  $c=4.1750(3)$  Å, respectively), with main structural characteristic the substitutional disorder observed at the R crystallographic site. The same structure is formed from the  $\text{Gd}_3(\text{Fe,Ti})_{29}$  when it is annealed at 1123 K ( $a=4.9044$  Å,  $c=4.1920$  Å). The compounds with  $R=\text{Gd}$  ( $\text{TM}=\text{V}$ ) crystallizes in a disordered  $\text{Th}_2\text{Zn}_{17}$  structure type (S.G.:  $R-3m$ ,  $a=8.5197(3)$  Å and  $c=12.481(1)$  Å) and with  $R=\text{Er}$  in a disordered  $\text{Th}_2\text{Ni}_{17}$  structure type (S.G.:  $P6_3/mmc$ ,  $a=8.4142(6)$  Å and  $c=8.3319(7)$  Å). A structural study of the  $\text{Y}_3(\text{Fe,V})_{29}$  compound based on time of flight, high resolution neutron powder diffraction data is presented. The magnetocrystalline anisotropy is of an easy plane type at room temperature for all the examined compounds. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Intermetallic compounds; Structure; Disorder; Neutron diffraction

## 1. Introduction

When the  $R_3(\text{Fe, TM})_{29}$  compounds, with  $R=\text{Y, Ce, Nd, Pr, Sm, Gd, Tb, Dy}$  and  $\text{TM}=\text{Ti}$  or other non-Fe transition metal element, are prepared by arc melting and annealed at a temperature of about 1273 K, they form the  $\text{Nd}_3(\text{Fe, Ti})_{29}$  structure type [1,2]. In an attempt to investigate if the phase diagram between 1123 and 1233 K gives the same or another structure type for heavy rare-earth elements or Y we study the  $R_3(\text{Fe,V})_{29}$  ( $R=\text{Dy, Er, Y}$ ) and  $\text{Gd}_3(\text{Fe, T})_{29}$  ( $T=\text{Ti, V}$ ) compounds. Detailed structural and magnetic studies of the  $R_3(\text{Fe,V})_{29}$  ( $R=\text{Dy, Y}$ ) compounds, annealed at 1123 K, have already been published in Refs. [3,4]. Rietveld analysis on X-ray powder diffraction data of these compounds shows that they crystallize in a disordered  $\text{CaCu}_5$ -type structure with stoichiometries  $\text{Y}_{1.0}(\text{Fe,V})_{9.5}$  (or  $\text{Y}_{3.0}(\text{Fe,V})_{28.5}$ ) and  $\text{Dy}_{1.0}(\text{Fe,V})_{9.9}$  (or  $\text{Dy}_{3.0}(\text{Fe,V})_{29.7}$ ) whereas their magnetocrystalline anisotropy is of an easy-plane type. In the present work a new structural study is presented for the  $\text{Y}_{1.0}(\text{Fe,V})_{9.5}$  compound which is based on the analysis of high resolution

neutron powder diffraction (NPD) spectra. Also the  $\text{Gd}_3(\text{Fe, TM})_{29}$ , with  $\text{TM}=\text{Ti}$  and  $\text{V}$ , and  $\text{Er}_3(\text{Fe,V})_{29}$  compounds, annealed at 1123 K, are studied.

## 2. Experimental

Ingots were prepared by arc melting the high purity (99.9%) constituents with nominal compositions:  $\text{Y}_3\text{Fe}_{27.5}\text{V}_{1.5}$ ,  $\text{Gd}_3\text{Fe}_{27.5}\text{Ti}_{1.5}$ ,  $\text{Gd}_3\text{Fe}_{27.5}\text{V}_{1.5}$ ,  $\text{Er}_3\text{Fe}_{28}\text{V}_1$ . Post-annealing has been performed in vacuum for 3 days at temperatures of: 1123 K for  $\text{Y}_3\text{Fe}_{27.5}\text{V}_{1.5}$ , 1123 K for  $\text{Gd}_3\text{Fe}_{27.5}\text{Ti}_{1.5}$ , 1073 K, 1123 K and 1173 K for  $\text{Gd}_3\text{Fe}_{27.5}\text{V}_{1.5}$  and  $\text{Er}_3\text{Fe}_{28}\text{V}_1$ . The samples were characterized by X-ray powder diffraction (XRD) using a Siemens D500 diffractometer with secondary graphite monochromator and  $\text{Cu K}\alpha$  radiation. Neutron powder diffraction measurements were performed at room temperature (RT) in the high resolution powder diffractometer (HRPD) at the neutron spallation source ISIS, Rutherford Appleton Laboratory, UK. Thermomagnetic analysis (TMA) was performed using a heating rate of  $5^\circ\text{C min}^{-1}$ , and the magnetic properties were studied with a Quantum Design

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SQUID magnetometer by applying a maximum field of 5 Tesla at RT.

### 3. Results and discussion

Several samples of  $Y_3Fe_{27.5}V_{1.5}$ ,  $Gd_3Fe_{27.5}Ti_{1.5}$ ,  $Gd_3Fe_{27.5}V_{1.5}$  and  $Er_3Fe_{28}V_1$  were prepared at different annealing temperatures whereas only the samples with optimum 3:29 composition, obtained at 1123 K, were studied. However, all the studied samples exhibit traces of the  $\alpha$ -Fe phase. The TMA measurements show a single Curie temperature of 527 and 408 K for the  $Gd_3Fe_{27.5}V_{1.5}$  (Fig. 1) and  $Er_3Fe_{28}V_1$  (Fig. 1) samples, respectively. For the  $Gd_3Fe_{27.5}Ti_{1.5}$  compound, a minor 1:12 phase (Fig. 1, at 614 K) was detected in addition to the major phase with a Curie temperature of 525 K. The  $Y_{3.0}Fe_{27.5}V_{1.5}$  sample, used in the NPD measurements, has the disordered  $CaCu_5$ -type phase [3] and its magnetic properties were shown elsewhere [3].

The analysis of the NPD was performed with the FULLPROF program [5]. Details for the analysis of the spectra measured from the backscattering data bank at  $2\theta=168.33^\circ$  are presented. The data were normalized and corrected for absorption. The structure reported in Ref. [3] was used as a starting model. The measurements of the NPD spectra were performed at RT, which is well below the Curie temperature [3] of 493 K. However, the examined high-resolution ( $\Delta d/d \approx 10^{-3}$ ) region of the time of flight spectrum (Fig. 2) includes d-spacings smaller than 0.23 nm, where the contribution of magnetic intensity is negligibly small.

As seen in Fig. 2, the Bragg peaks were indexed with a disordered  $CaCu_5$  type structure, and a secondary phase of

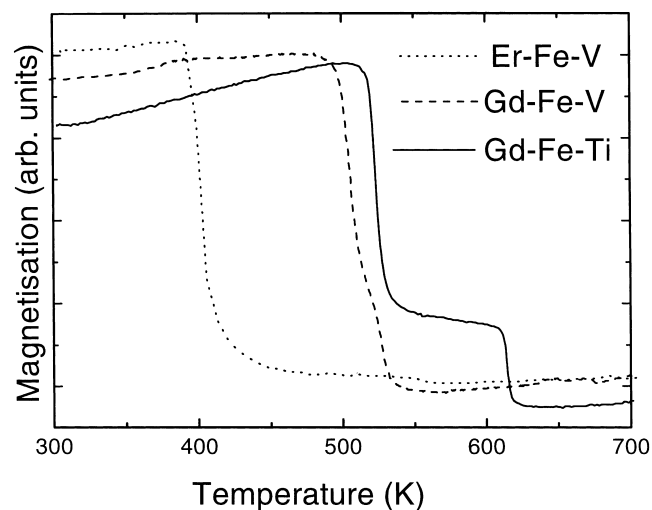


Fig. 1. Thermomagnetic measurements for  $Gd_{3.0}Fe_{27.5}TM_{1.5}$  with TM = Ti ( $T_C=525$  K major phase,  $T_C=614$  K for minor 1:12 phase) and TM = V ( $T_C=527$  K) and  $Er_3Fe_{28}V_1$  ( $T_C=408$  K) samples annealed at 1123 K.

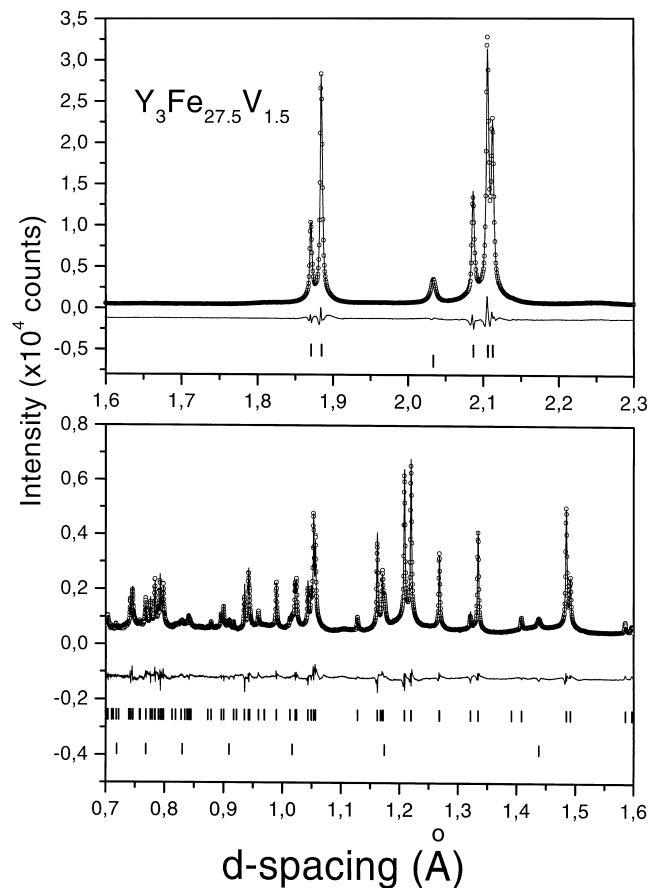


Fig. 2. The observed, calculated and difference neutron time-of-flight diffraction patterns at room temperature, for the  $Y_3Fe_{27.5}V_{1.5}$  compound annealed at 1123 K. Vertical bars indicate the position of Bragg peaks for the disordered  $CaCu_5$  type structure and the  $\alpha$ -Fe phase.

$\alpha$ -Fe. Detailed macroscopic studies of the magnetic properties, especially those concerning the magnetocrystalline anisotropy have shown that the anisotropy is of an easy plane type [3,6], or that the moments of magnetic atoms are aligned within the ( $a,b$ ) crystallographic plane of the hexagonal cell. Calculations based on the value of the saturation magnetization at RT ( $125.5 \text{ Am}^2 \text{ kg}^{-1}$ ) give an average magnetic moment per iron atom equal to  $1.53 \mu_B$ . Measurements based on  $^{57}\text{Fe}$  Mössbauer spectroscopy [7] of the series of  $Y_3Fe_{29-x}V_x$  compounds, that adopt the  $Nd_3(Fe,Ti)_{29}$  type structure, give a value of  $14.5 \text{ T}/\mu_B$  for the ratio of the average hyperfine field (B-hf) per magnetic moment of iron atoms. Since the average hyperfine field for the compound under study is 21.5 T at 300 K [3] then an average value of  $1.48 \mu_B$  is deduced per iron atom, which is in agreement with that derived from saturation magnetization measurements. Thus, the average magnetic moment of  $1.51 \mu_B$  has been used for each iron atom, lying along the hexagonal  $a$ -axis, and it was kept constant through all the stages of the refinement. The final values for the crystallographic parameters are given in Table 1. Any attempt to locate the crystallographic site of vanadium stabilizing element was not successful. Comparatively, in

Table 1

Crystallographic data for the  $Y_3(Fe,V)_{29}$  compound with the disordered  $CaCu_5$ -type structure (space group  $P6/mmm$ , No. 191)<sup>a</sup>

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )	Occupancy
Y	1a	0.0	0.0	0.0	1.08(7)	0.619(4)
		0.0	0.0	0.0	0.6	0.610(2)
Fe(1)	2c	0.33333	0.66667	0.0	1.44(4)	0.30(3)
		0.33333	0.66667	0.0	1.5(1)	0.775(11)
Fe(2)	3g	0.5	0.0	0.5	1.08(2)	1.0
		0.5	0.0	0.5	0.82(6)	1.0
Fe(3)	2e	0.0	0.0	0.2830(7)	2.28(8)	0.383(2)
		0.0	0.0	0.288(1)	0.9(1)	0.390(2)
Fe(4)	6l	0.283(2)	0.566(2)	0.0	1.44(4)	0.232(8)
		0.270(3)	0.540(6)	0.0	1.5(1)	0.075(4)

<sup>a</sup> For every element there are two rows: the first corresponds to results derived from the present refinement of neutron data and the second row are results given in Ref. [13] for comparison. Neutron data:  $a=4.87837(5)$  Å,  $c=4.17322(5)$ ,  $V=86.010(2)$  Å<sup>3</sup>. *R* factors:  $R_{wp}=5.82$ ,  $R_{exp}=1.28$ ,  $R_B(\text{nuclear})=3.61$ ,  $R_{magnetic}=4.82$ . X-ray data:  $a=4.8769(1)$  Å,  $c=4.1728(3)$ ,  $V=85.95$  Å<sup>3</sup>. *R* factors:  $R_p=5.45$ ,  $R_{wp}=8.61$ ,  $R_B=5.55$ ,  $R_{exp}=2.69\%$ .

Table 1 are listed the values of the corresponding parameters from the XRD data analysis [3]. The formula units derived from the analysis of the two data sets are:  $Y_{0.619}(F,V)_{5.77}$  or  $Y_{1.0}(F,V)_{9.32}$  (neutron data) and  $Y_{0.607}(F,V)_{5.78}$  or  $Y_{1.0}(F,V)_{9.5}$  (XRD). The  $\alpha$ -Fe content for the sample studied with NPD was 4% (8% from XRD). The most remarkable difference between the two models concerns the occupancies of the crystallographic sites 2c and 6l (Fe(1) and Fe(4) atoms). The NPD data analysis gives a higher occupancy for the 6l sites, which are the disordered sites of iron atoms surrounding the dumb-bell sites. This result supports the suggested [3] structural model for this type of compounds where 39% of Y atoms are substituted by dumb-bell iron atoms. However, the high resolution of the NPD spectrum in the small d-spacing range permits a more accurate estimation of the Fe occupancies at 6l sites.

In the following we examine the dependence of phase formation for  $Gd_3Fe_{27.5}TM_{1.5}$  on non-magnetic  $TM=Ti$  or  $V$  elements. The Rietveld analysis of the  $Gd_3Fe_{27.5}Ti_{1.5}$  compound is in agreement with TMA results, both indicating that this sample consists of two phases. The main phase (72% according to Rietveld analysis) crystallizes in the  $P6/mmm$  space group and has the disordered  $CaCu_5$  type structure whereas the second phase forms the  $Gd(Fe,Ti)_{12}$  structure (28%). The structural model for the major phase is like the one used for  $Y_3(Fe,V)_{29}$  [3]. The lattice parameters for this phase are:  $a=4.90435(7)$  Å,  $c=4.1920(2)$  Å,  $V_{cell}=87.32$  Å<sup>3</sup>. The occupancy of the Gd-1a site is 0.619, of the Fe(1)-2c site is 0.53, of the Fe(2)-3g site is 1.0, of the Fe(3)-2e site (or dumb-bell site) is 0.407 and of the Fe(4)-6l site is 0.16. The stoichiometric formula calculated from these occupation factors is:  $Gd_{0.619}(Fe,Ti)_{5.814}$  or  $Gd_{1.0}(Fe,Ti)_{9.39}$  or  $Gd_{3.0}(Fe,Ti)_{28.2}$ . The variable coordinates are  $z(2e)=0.289(2)$  and  $x(6l)=0.269(5)$ . The reliability factors are:  $R=7.68$ ,  $R_{wp}=9.25$ ,  $R_{exp}=3.44$ ,  $R_B(Gd_3(Fe,Ti)_{29})=4.93\%$  and  $R_B(Gd_1(Fe,Ti)_{12})=8.62\%$ .

The Rietveld analysis of the  $Gd_3Fe_{27.5}V_{1.5}$  sample, annealed at 1123 K, gives the best fitting for the  $R-3m$

space group of a disordered  $Th_2Zn_{17}$  type structure. The unit cell dimensions are:  $a=8.5197(3)$  Å,  $c=12.481(1)$  Å and  $V_{cell}=784.59$  Å<sup>3</sup>. This structure-type is also formed by the  $RFe_7$  ( $R=Ce, Pr, Nd$  and  $Sm$ ) compounds [8]. In this model a statistically occupied (18%) 3a site (0,0,0) of Gd atoms is required in addition to the usual crystallographic sites observed in the ordered  $Th_2Zn_{17}$  type structure [8]. The dumb-bell iron sites (6c) are also statistically occupied (82%). The  $\alpha$ -Fe content is about 7%. The calculated stoichiometric formula obtained by the Rietveld method is:  $Gd_{6.55}(Fe,V)_{49.89}$  or  $Gd_1(Fe,V)_{7.62}$ . Besides the effect of the annealing temperature [9], for the formation of  $GdFe_{8.5}$  stoichiometry in the  $Th_2Zn_{17}$  or the  $Th_2Ni_{17}$  or the  $CaCu_5$  disordered structures, we have shown that the variation of Ti or V concentrations produce similar structural disorder.

The  $R_3(Fe,V)_{29}$  compounds with  $R=Y, Gd, Dy$  form the  $Nd_3(Fe,Ti)_{29}$  type structure with proper heat treatment [1]. On the other hand, we examine the heavy rare earth  $Er_3Fe_{28}V_1$  compound, which is known that does not form this structure type. In this study all the Er based samples exhibit the same phase composition. The Rietveld analysis for the sample annealed at 1123 K, gives a disordered  $Th_2Ni_{17}$  structure type ( $P6_3/mmc$  space group) that has been observed for the  $R_2Fe_{17}$  intermetallic compounds with heavy rare earths and Y ( $R=Ho$  [10], Lu [11] and Y [12]). The unit cell dimensions are:  $a=8.4142(2)$  Å,  $c=8.3319(7)$  Å and  $V_{cell}=510.87$  Å<sup>3</sup>. The Ho, Lu and Y compounds exhibit an extensive disorder. The disorder in  $Er_3Fe_{28}V_1$  is restricted in the statistical occupation (76%) of the 2b site by Er and the statistical occupation (49%) of the 4e dumb-bell site by Fe. The  $\alpha$ -Fe content is about 10%. The calculated stoichiometric formula obtained by the Rietveld method is:  $Er_{3.51}(Fe,V)_{34.98}$  or  $Er_{1.0}(Fe,V)_{9.97}$ .

A detailed presentation of magnetic properties is given in Refs. [3,4] for the  $R_3(Fe,V)_{29}$  ( $R=Dy, Y$ ) with the disordered  $CaCu_5$ -type structure. In this study, magnetization measurements of the  $Gd_3Fe_{27.5}Ti_{1.5}$  sample give a saturation magnetization of 94.3 emu g<sup>-1</sup> at 300 K. This value has been derived by taking into account the 1:12 phase content from the Rietveld analysis. XRD measure-

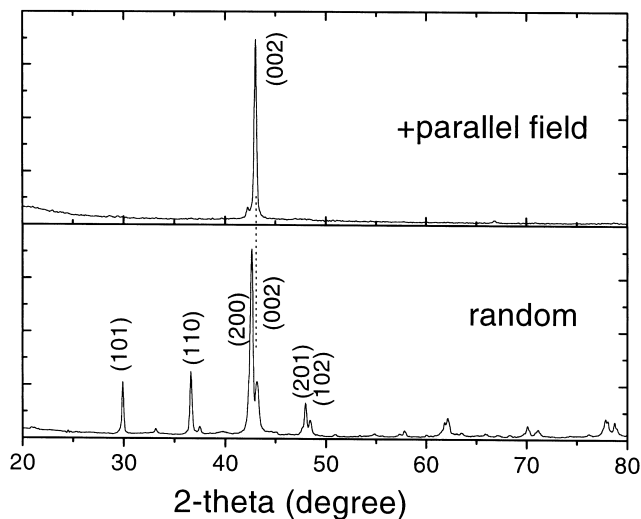


Fig. 3. XRD spectra for random (a) and magnetically aligned (b) powder for  $\text{Gd}_3\text{Fe}_{27.5}\text{Ti}_{1.5}$  compound. In (b), the aligned magnetic field was parallel to the sample holder.

ments at 300 K (Fig. 3) on a magnetically oriented sample, with the magnetic field applied parallel to the sample holder surface, show that only the reflections with Miller indices (001) remain intense. This means that the magnetocrystalline anisotropy is of an easy plane type as in  $\text{R}_3(\text{Fe,V})_{29}$  ( $\text{R}=\text{Dy}, \text{Y}$ ) case, where the disordered  $\text{CaCu}_5$  structure [3,4] appears.

In  $\text{Gd}_3\text{Fe}_{27.5}\text{V}_{1.5}$  (disordered  $\text{Th}_2\text{Zn}_{17}$ ) and  $\text{Er}_3\text{Fe}_{28}\text{V}_1$  (disordered  $\text{Th}_2\text{Ni}_{17}$ ) samples, the  $T_C$  values (Fig. 1) of 527 and 408 K, respectively, are higher than the corresponding values of  $\text{Gd}_2\text{Fe}_{17}$  (477 K for  $\text{Th}_2\text{Zn}_{17}$  type structure [13]) and  $\text{Er}_2\text{Fe}_{17}$  (296 K for  $\text{Th}_2\text{Ni}_{17}$  type structure [13]), due to vanadium concentration in these phases. Concerning the magnetic anisotropy, XRD measurements on magnetically aligned samples indicate that  $\text{Gd}_3\text{Fe}_{27.5}\text{V}_{1.5}$  and  $\text{Er}_3\text{Fe}_{28}\text{V}_1$  samples exhibit an easy plane type magnetocrystalline anisotropy as the corresponding  $\text{Gd}_2\text{Fe}_{17}$  and  $\text{Er}_2\text{Fe}_{17}$  phases [14].

#### 4. Conclusions

Annealing of the  $\text{R}_3(\text{Fe,V})_{29}$  ( $\text{R}=\text{Dy}, \text{Er}, \text{Y}$ ) and  $\text{Gd}_3(\text{Fe}, \text{T})_{29}$  ( $\text{T}=\text{Ti}, \text{V}$ ) compounds at 1123 K produces a variety of phases that crystallize in the disordered  $\text{CaCu}_5$  ( $\text{R}=\text{Dy}, \text{Y}$  and  $\text{Gd}$  with  $\text{T}=\text{Ti}$ ), the disordered  $\text{Th}_2\text{Zn}_{17}$  ( $\text{R}=\text{Gd}, \text{T}=\text{V}$ ) and disordered  $\text{Th}_2\text{Ni}_{17}$  ( $\text{R}=\text{Er}$ ) type structures. In  $\text{Y}_3(\text{Fe,V})_{29}$  compound a structural study based on high resolution NPD spectrum reveals a higher

Fe occupancy of the disordered 6l site relative to previous [3] analysis of X-ray powder diffraction data. The phase formation of the studied Gd compound, except from the annealing temperature, is influenced by the presence of Ti or V. All the studied samples show a magnetocrystalline anisotropy of an easy plane type at room temperature as the 2:17 compounds [14].

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