

## VIOLARITE STABILITY RELATIONS

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## ABSTRACT

Violarite,  $\text{FeNi}_2\text{S}_4$ , a member of the spinel-sulfide groups, has a maximum thermal stability of  $461 \pm 3^\circ\text{C}$  in the Fe-Ni-S system. Violarite solid solution extends toward more Ni-rich compositions at lower temperatures becoming complete with  $\text{Ni}_3\text{S}_4$  at  $356^\circ\text{C}$ . The unit cell varies from  $9.465 \pm 0.003\text{\AA}$  for  $\text{FeNi}_2\text{S}_4$  to  $9.489 \pm 0.003\text{\AA}$  for  $\text{Ni}_3\text{S}_4$ . It is likely that much hypogene violarite is formed by exsolution from initially deposited  $(\text{Fe, Ni})_{1-x}\text{S}$  monosulfide solid solution.

## INTRODUCTION

Violarite,  $\text{FeNi}_2\text{S}_4$ , one of the less common iron-nickel sulfides, is a member of the spinel sulfide mineral series,  $M_3\text{S}_4$  (where  $M = \text{Fe, Ni, Co, Cu, Cr}$ ). Although rarely constituting a major component of nickel-bearing ores, it is commonly present in small amounts, especially where weathering of pentlandite by meteoric waters has occurred. Typically such occurrences are in pyrrhotite-rich sulfide ores associated with ultramafic intrusives such as those at Sudbury, Ontario and Marbridge, Quebec.

## PREVIOUS WORK

Violarite was originally described by Lindgren and Davy (1924), who suggested from analyses of contaminated samples, a composition of  $\text{NiS}_2$ . Short and Shannon (1930), on the basis of new analyses, proposed the now accepted formula of  $\text{FeNi}_2\text{S}_4$ . Tarr (1935) compiled all available analyses of the spinel-sulfide minerals and concluded that in spite of the frequent association of violarite with polydymite ( $\text{Ni}_3\text{S}_4$ ) and the similarity of their compositions, the two minerals were distinct.

The first synthesis of violarite was reported by Lundqvist (1947), who reacted S with Fe-Ni filings in evacuated glass tubes. He observed violarite at  $200^\circ\text{C}$ , but not at  $480^\circ\text{C}$  and above, noting ". . . it is not obvious whether this phase is a ternary phase separated from  $\text{Ni}_3\text{S}_4$  through a two-phase area, or if it is linked with this phase . . . there are some facts which suggest that the phase with iron content has properties different from  $\text{Ni}_3\text{S}_4$ ." Kullerud (1963) in his extensive study of the Fe-Ni-S system did not observe a violarite phase at  $400^\circ\text{C}$  or above. Craig (1968) reported preliminary findings on the phase relations involving violarite; that work has been expanded in the present paper.

## EXPERIMENTAL REACTANTS AND PROCEDURES

Experiments were prepared using iron, nickel, and sulfur of 99.999+ percent purity as indicated by suppliers analyses. Oxide films on the metal powders were removed by reduction in a stream of hydrogen at 700°C for eight hours prior to use. Experimental charges were prepared in evaluated fused quartz tubes which were heated in muffle furnaces in which the temperature was maintained  $\pm 2^\circ\text{C}$ . At the termination of each experiment, the charges were rapidly cooled by immersion in ice water. The reaction products were analyzed by X-ray diffraction and reflection microscopic techniques.

## EXPERIMENTAL RESULTS AND DISCUSSION OF SYNTHESIS

Violarite was first encountered by accident during experiments at 300° and 400°C designed to define the composition limits of the monosulfide solid solution (Mss) in the central portion of the Fe-Ni-S system. Starting with Mss compositions near the sulfur-rich limit at 600°C, it was expected that annealing at 300°C or 400°C, would result in exsolution of pyrite ( $\text{FeS}_2$ ) and/or vaesite ( $\text{NiS}_2$ ). In addition, however, several percent of fine lamellar laths of a light violet-gray phase, subsequently identified as violarite, also appeared. Attempts to synthesize violarite of  $\text{FeNi}_2\text{S}_4$  composition by direct reaction of iron, nickel, and sulfur at 300° and 400°C were futile and resulted in formation of variable but large percentages of pyrite, vaesite, and Mss with but traces of violarite. Repeated regrinding of these charges over periods of several months increased the violarite content to only a few percent. The immediacy with which the metastable assemblage of pyrite, vaesite, and Mss formed and the very slow rate at which these phases then reacted to form violarite possibly explains why Kullerud (1963) did not obtain violarite in his experiments at 400°C.

To circumvent the rapid formation and metastable preservation of pyrite and vaesite, a two-step process was employed in violarite synthesis. (1) Preparation of an Mss containing Fe and Ni in 1:2 atomic proportions, by direct reaction of the elements at 500° to 700°C; one grinding followed by heating for two to three additional days was usually sufficient for homogenization; (2) Reaction at 200° to 300°C of this finely ground Mss, with the appropriate amount of sulfur to achieve the  $\text{FeNi}_2\text{S}_4$  composition for five to ten days. Best results, producing 95 to 100 percent violarite, were achieved when the Mss and the sulfur were physically separated by silica wool, thus limiting the reaction to sulfur transported in the vapor state. At 400°C this second step resulted in formation of considerable amounts of pyrite because of the extension of pyrite-Mss tie lines (as noted in Figure 1c) between Mss of Fe:Ni=1:2 atomic proportions and  $\text{FeNi}_2\text{S}_4$ . As with attempts of direct one step syntheses, pyrite once formed broke down only slowly.

Employment of the two-step synthesis permitted preparation of homogeneous  $M_3S_4$  compositions between  $\text{FeNi}_2\text{S}_4$  and  $\text{Fe}_{0.25}\text{Ni}_{2.75}\text{S}_4$ . Attempts to synthesize homogeneous  $M_3S_4$  compositions more nickel-rich than  $\text{Fe}_{0.25}\text{Ni}_{2.75}\text{S}_4$  resulted in formation of 10 to 20 percent  $\text{NiS}_2$  and residual Mss in addition to the spinel phase; this probably resulted from sluggishness of formation of the spinel phase and buildup of the sulfur vapor pressure to a degree sufficient to nucleate vaesite.

## VIOLARITE RELATIONS AND STABILITY

Once a satisfactory method for violarite synthesis was found, it was possible to examine the relations surrounding this phase and its thermal stability. The results of these investigations between 500° and 300°C are noted in Figure 1; selected experiments defining the assemblages shown in Figure 1 are given in Table 1. The compositions of the pyrite, (Fe,

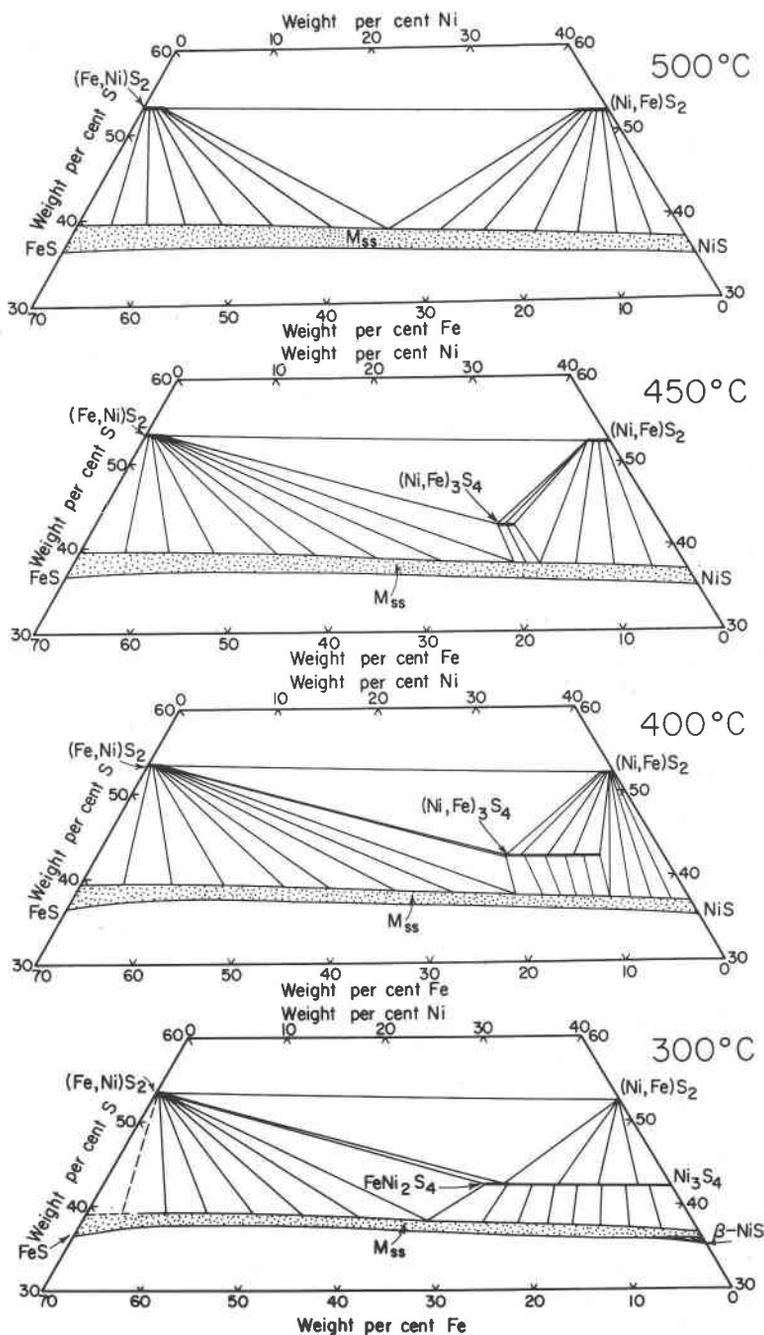


FIG. 1. Phase relations involving the appearance of violarite and development of the violarite-polydymite solid solution at: A-500°C, B-450°C, C-400°C, D-300°C.

TABLE 1. EXPERIMENTS DEFINING PHASE RELATIONS SURROUNDING THE  $\text{FeNi}_2\text{S}_4\text{-Ni}_3\text{S}_4$  SOLID SOLUTION

Exp. No.	Composition, wt. %			Reactants <sup>a</sup>	Temp. °C	Time Days	Products
	Fe	Ni	S				
496	29.8	30.7	39.5	Mss+vs(tr.)	500	26	Mss+py+vs
497	30.0	31.0	39.0	Mss	500	26	Mss+py
498	30.3	31.2	38.5	Mss	500	26	Mss
569	25.0	35.5	39.5	Mss+vs(tr.)	500	26	Mss+vs
605	20.0	41.0	39.0	Mss+vs(tr.)	450	30	Mss+py+vs(tr.)
596	16.0	45.0	39.0	Mss+vs(tr.)+viol(tr.)	450	37	Mss+viol+py
561	12.0	50.0	38.0	Mss+vs(tr.)	450	43	Mss+vs
309	20.0	41.0	39.0	Mss+vs(tr.)	400	170	Mss+py
572	16.0	45.0	39.0	Mss+vs(tr.)	400	38	Mss+viol+vs(tr.)
611	11.4	49.6	39.0	Mss+S	400	77	Mss+viol
494	6.0	55.5	38.5	Mss+vs(tr.)	400	29	Mss+vs
474	29.8	30.7	39.5	Mss+vs(tr.)	300	34	Mss+py
571	25.0	35.5	39.5	Mss+vs(tr.)	300	38	Mss+viol
480	20.0	41.0	39.0	Mss+vs(tr.)	300	34	Mss+viol
548	12.0	50.0	38.0	Mss	300	60	Mss+viol
487	6.0	55.5	38.5	Mss+vs(tr.)	300	33	Mss+viol

<sup>a</sup> tr. indicates trace

$\text{NiS}_2$ , and vaesite,  $(\text{Ni, Fe})\text{S}_2$ , have been taken from Clark and Kullerud (1963) who extrapolated data from higher temperature studies. It is noteworthy that violarite bearing assemblages may contain as little as 5 weight percent Ni.

The maximum thermal stability of violarite in the presence of an equilibrium vapor is  $461 \pm 3^\circ\text{C}$ , at which temperature it decomposes to form  $(\text{Fe, Ni})\text{S}_2$ ,  $(\text{Ni, Fe})\text{S}_2$  and Mss containing Fe and Ni in the atomic ratio 1:2.4. As noted in Figure 2a, a section along the  $\text{FeNi}_2\text{S}_4\text{-Ni}_3\text{S}_4$  join, the composition with maximum thermal stability is  $\text{Fe}_{0.92}\text{Ni}_{2.08}\text{S}_4$ . Below  $461^\circ\text{C}$  the violarite solid solution expands to reach  $\text{FeNi}_2\text{S}_4$  at  $356 \pm 3^\circ\text{C}$ , the upper stability of polydymite (Kullerud and Yund, 1962). Homogeneous  $\text{FeNi}_2\text{S}_4\text{-Ni}_3\text{S}_4$  solid solutions were synthesized at  $200^\circ\text{C}$  and it was found that previously prepared compositions did not break down when heated at  $200^\circ\text{C}$  for periods up to six months.

Combination of  $\text{S}_2$  vapor pressure data for the  $\text{py} + \text{vs} + \text{Mss}$  assemblage at  $600^\circ\text{C}$  ( $10^{-1.8}$  atm) from Naldrett and Craig (1968), and for the  $\text{py} + \text{viol} + \text{Mss}$  assemblage at  $450^\circ$  ( $10^{-4.8}$  atm) and  $400^\circ$  ( $10^{-6.0}$  atm) from Craig and Naldrett (1971) with an estimated entropy for  $\text{FeNi}_2\text{S}_4$  of  $S_{298} = 46.0^1$  permit formulation of the free energy equation for formation of violarite as:

<sup>1</sup>  $S_{299} = 46.0$  is the average value obtained from Latimer's (1951) and Grønvald and Westrum's (1962) approximations and the reactions  $\text{FeS}_2 + 2\text{NiS} = \text{FeNi}_2\text{S}_4$  and  $\text{FeS} + \text{NiS} + \text{NiS}_2 = \text{FeNi}_2\text{S}_4$  assuming  $\Delta S$  for these reactions is 0. The free energy equations given in the text assume that  $\Delta S$  and  $\Delta H$  for the formation of  $\text{FeNi}_2\text{S}_4$  are temperature independent.

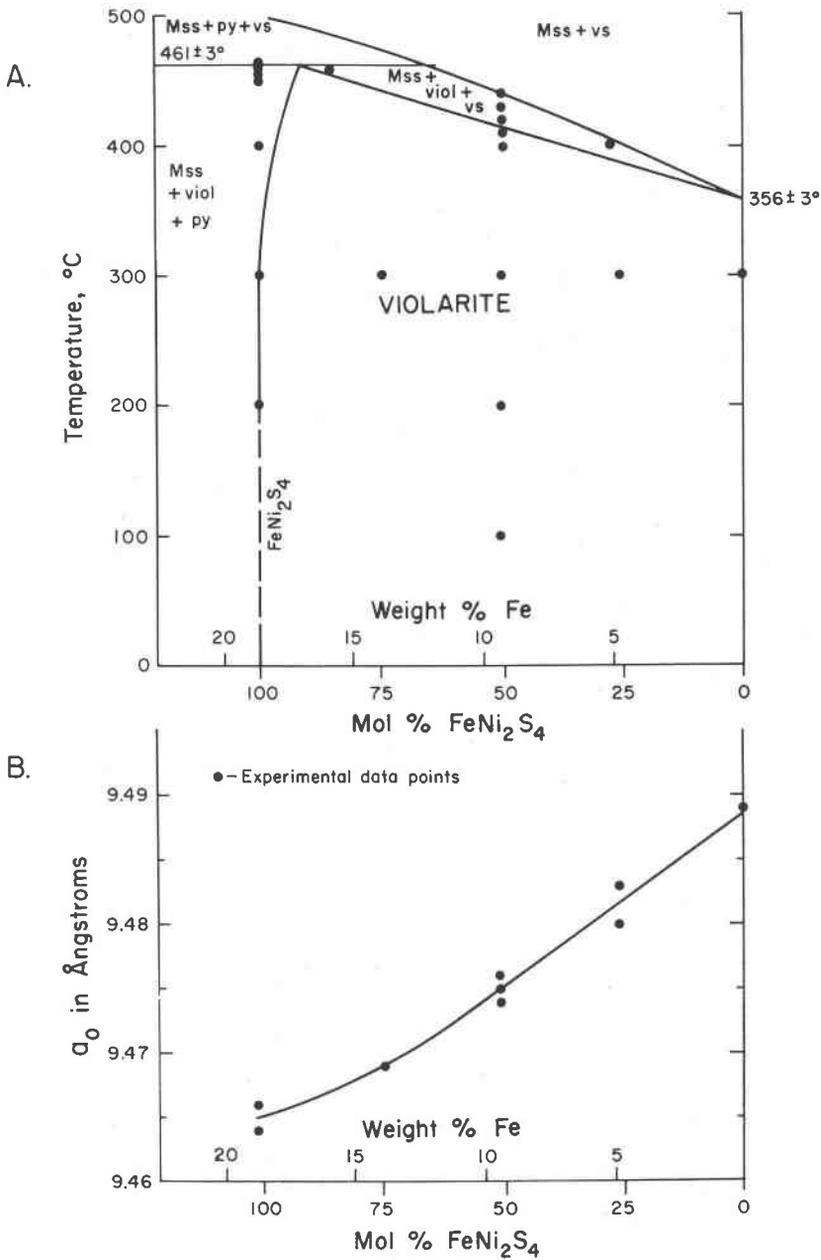
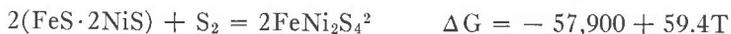
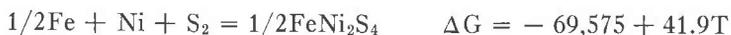


FIG. 2. A. Section along the  $\text{FeNi}_2\text{S}_4$ - $\text{Ni}_3\text{S}_4$  join. B. Variation of unit cell parameter with variation in composition along the  $\text{FeNi}_2\text{S}_4$ - $\text{Ni}_3\text{S}_4$  join.



(T is degrees Kelvin).

#### X-RAY DATA

Violarite and polydymite belong to the spinel series ( $M_3S_4$ ) of sulfide minerals which crystallize in the space group  $Fd3m$ . The variation in the unit cell from the  $\text{FeNi}_2\text{S}_4$  value of  $9.465 \pm 0.003\text{\AA}$  to the  $\text{Ni}_3\text{S}_4$  value of  $9.489 \pm 0.003\text{\AA}$  is shown in Figure 2b. Values were measured with a diffractometer using nickel filtered Cu radiation, and silicon as an internal standard.

Naturally occurring violarites commonly contain 0.1 to 7.0 weight percent cobalt substituting for iron and nickel.  $\text{Co}_3\text{S}_4$  is isostructural with violarite and polydymite and has an  $a$  of  $9.43 \text{\AA}$  (Berry and Thompson, 1962), thus the substitution of Co into the violarite lattice will tend to reduce the unit cell dimension.

#### SPECULATIONS ON PHASE RELATIONS AT LOW TEMPERATURES

The low temperature phase relations involving violarite are uncertain. Kullerud *et al.*, (1969) suggested that the common occurrence of secondary violarite on weathering pentlandite may indicate a low temperature tie line between the phases. Buchans and Blowes (1968) and Naldrett (personal comm. 1970) on the other hand report hypogene pyrite-millerite intergrowths in ores from Marbridge, Quebec. A pyrite-millerite join would invalidate a stable join between violarite and pentlandite. The analyses of Buchans and Blowes (1968) indicate Fe-deficiency of the violarites and 1 to 2 percent Fe in solid solution in the millerite; these variations from  $\text{FeNi}_2\text{S}_4$  and NiS might be sufficient to permit stable pyrite-millerite tie lines.

The violarite and polydymite analyses listed by Tarr (1935) and by Buchans and Blowes (1968) reveal a bimodal distribution with Fe contents less than 3 percent and greater than 9 percent. However, co-existing violarite and polydymite, indicative of a solvus, have not been reported. Low temperature silica tube and precipitation experiments prepared with  $\text{FeSO}_4$ ,  $\text{NiSO}_4$ , and  $\text{Na}_2\text{S}$  solutions have thus far failed to yield data to support or refute the existence of a solvus.

#### GEOLOGICAL CONSIDERATIONS

Violarite, where encountered, has generally been considered a super-

<sup>2</sup> The  $\Delta S$  values in this equation takes into account the inversion of FeS and NiS to high temperature forms; thus it is only applicable in the temperature range  $379^\circ$  to  $461^\circ\text{C}$ .

TABLE 2. SYNTHESIS EXPERIMENTS ALONG  $\text{FeNi}_2\text{S}_4\text{-Ni}_3\text{S}_4$  JOIN

Exp. No.	Composition mol %		Reaction 1 <sup>a</sup>		Time Days	Reaction 2		Time Days	Products <sup>b</sup>	$t_{1/2}$
	$\text{FeNi}_2\text{S}_4$	$\text{Ni}_3\text{S}_4$	Reaction	T, °C		Reaction	T, °C			
	21	100	0	$\text{Fe} + \text{Ni} + \text{S} \rightarrow \text{Mss}$	500	19	$\text{Mss} + \text{S} \rightarrow \text{viol}$	300	67	viol
22	75	25	$\text{Fe} + \text{Ni} + \text{S} \rightarrow \text{Mss}$	500	19	$\text{Mss} + \text{S} \rightarrow \text{viol}$	300	67	viol	9.469
23	50	50	$\text{Fe} + \text{Ni} + \text{S} \rightarrow \text{Mss}$	500	19	$\text{Mss} + \text{S} \rightarrow \text{viol}$	300	67	viol	9.475
24	25	75	$\text{Fe} + \text{Ni} + \text{S} \rightarrow \text{Mss}$	500	19	$\text{Mss} + \text{S} \rightarrow \text{viol}$	300	67	viol	9.483
25	0	100	$\text{Ni} + \text{S} \rightarrow \text{Ni}_{1-x}\text{S}$	500	19	$\text{Ni}_{1-x}\text{S} + \text{S} \rightarrow \text{pm}$	300	67	$\text{pm} + \text{vs} + \text{Ni}_{1-x}\text{S}$	9.490
601	100	0	$\text{Fe} + \text{Ni} + \text{S} \rightarrow \text{Mss}$	600	4	$\text{Mss} + \text{S} \rightarrow \text{viol}$	400	12	$\text{Mss} + \text{py} + \text{viol}$	—
574	100	0	$\text{Fe} + \text{Ni} + \text{S} \rightarrow \text{M}_3\text{S}_4$	400	38	—	—	—	$\text{Mss} + \text{py} + \text{vs} + \text{viol}$	—

<sup>a</sup> Samples reacted 2 days, opened, ground, resealed; time indicates total days at Reaction 1 temperature.

<sup>b</sup> viol =  $\text{FeNi}_2\text{S}_4\text{-Ni}_3\text{S}_4$  solid solution

pm =  $\text{Ni}_3\text{S}_4$

py = pyrite

vs = vaesite

Mss =  $(\text{Fe, Ni})_{1-x}\text{S}$  solid solution

TABLE 3. STABILITY EXPERIMENTS ALONG  $\text{FeNi}_2\text{S}_4\text{-Ni}_3\text{S}_4$  JOIN

Exp. No.	Composition mol % $\text{FeNi}_2\text{S}_4$	T., °C	Time Days	Reactants	(in order of) (abundance)
579	100	300	31	Mss+S	viol
632	100	400	56	viol	viol+Mss+py
593	100	450	14	viol	viol+Mss+py
616	100	458	4	Mss+S	Mss+py+vs+viol
628	100	458	4	viol	viol+Mss+py
623	100	464	4	viol	Mss+vs+py
622	100	481	1	viol	Mss+vs+py
724	50	400	7	viol	viol
725-1	50	410	4	viol	viol
725-2	50	420	4	viol	viol+Mss+vs
777	50	430	6	viol	viol+Mss+vs
724-1	50	440	4	viol	Mss+vs
24-1	25	400	10	viol	viol+Mss+vs

gene mineral formed as the result of surficial alteration of iron-nickel sulfides, especially pentlandite. The present study demonstrates that violarite, stable below  $461 \pm 3^\circ\text{C}$  in the presence of an equilibrium vapor, may form as a hypogene phase by primary direct crystallization or by secondary exsolution from an initially homogeneous Mss phase. Violarite formation is not necessarily confined to Ni-rich environments, but may form as a hypogene mineral in ores containing as little as 5 percent nickel provided that a nickeliferous pyrite is present. Violarite formation through alteration of pentlandite may not represent an equilibrium assemblage, but only failure of the alternative pyrite-millerite assemblage to nucleate.

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