

# The Tribute of Pentavalent Molybdenum in $\text{LiEuMo}_2\text{O}_8$

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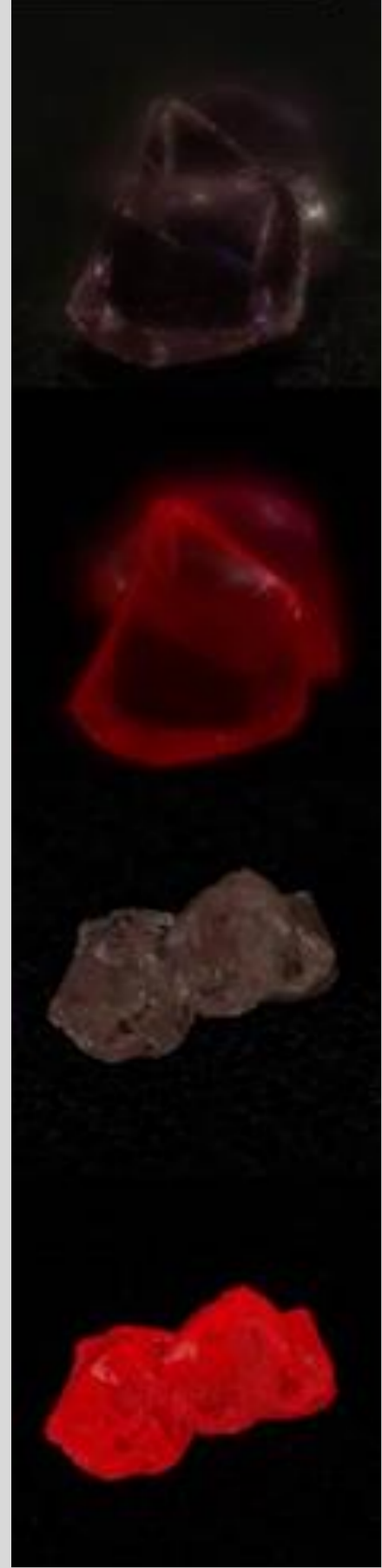
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## Background

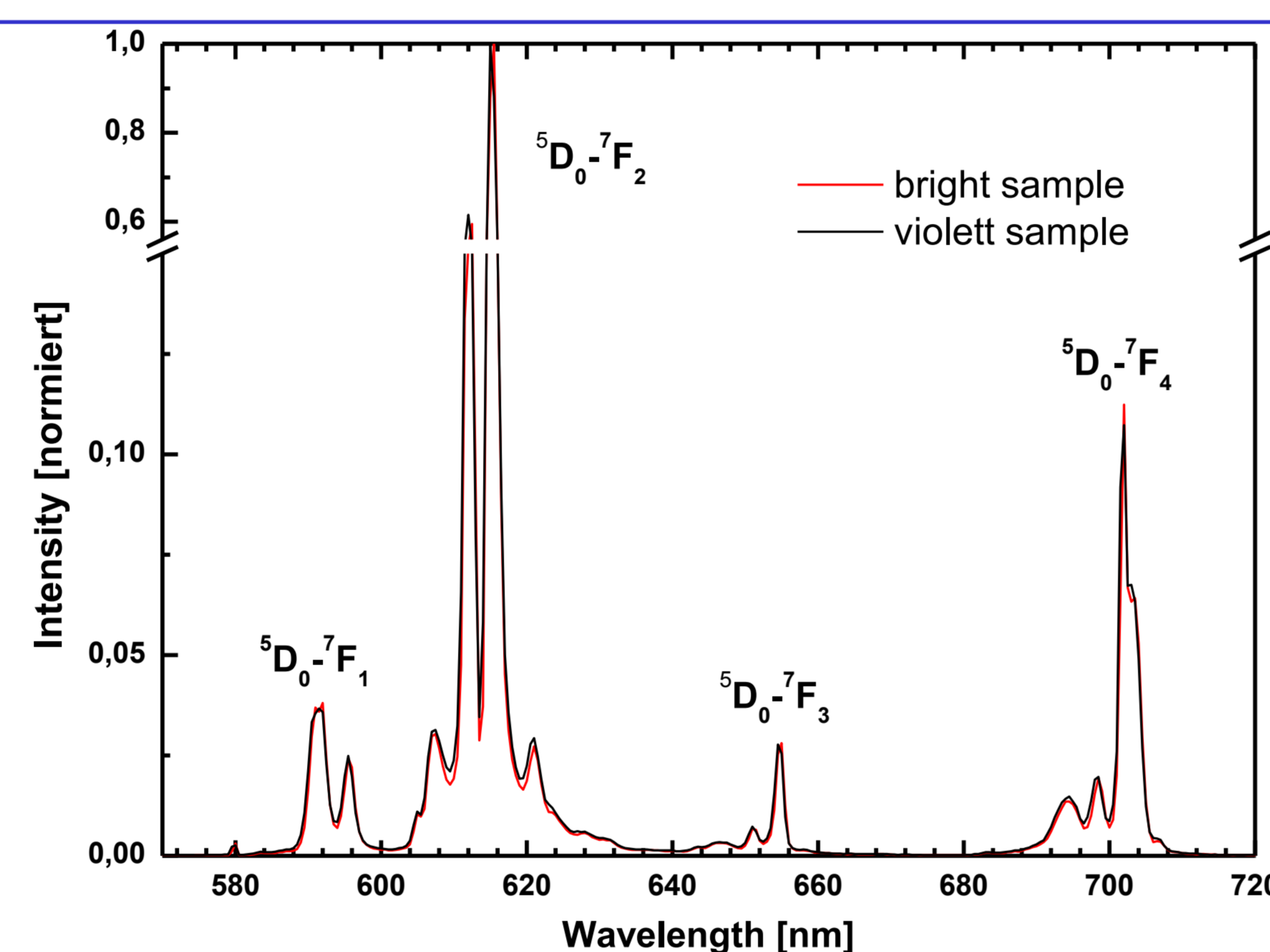
Bulk single crystals of  $\text{LiEuMo}_2\text{O}_8$  have been grown by top-seeded solution growth method. Surprisingly, the resulting crystals show variation in the color shade from a dark violet to a bright shining red (Fig.1).



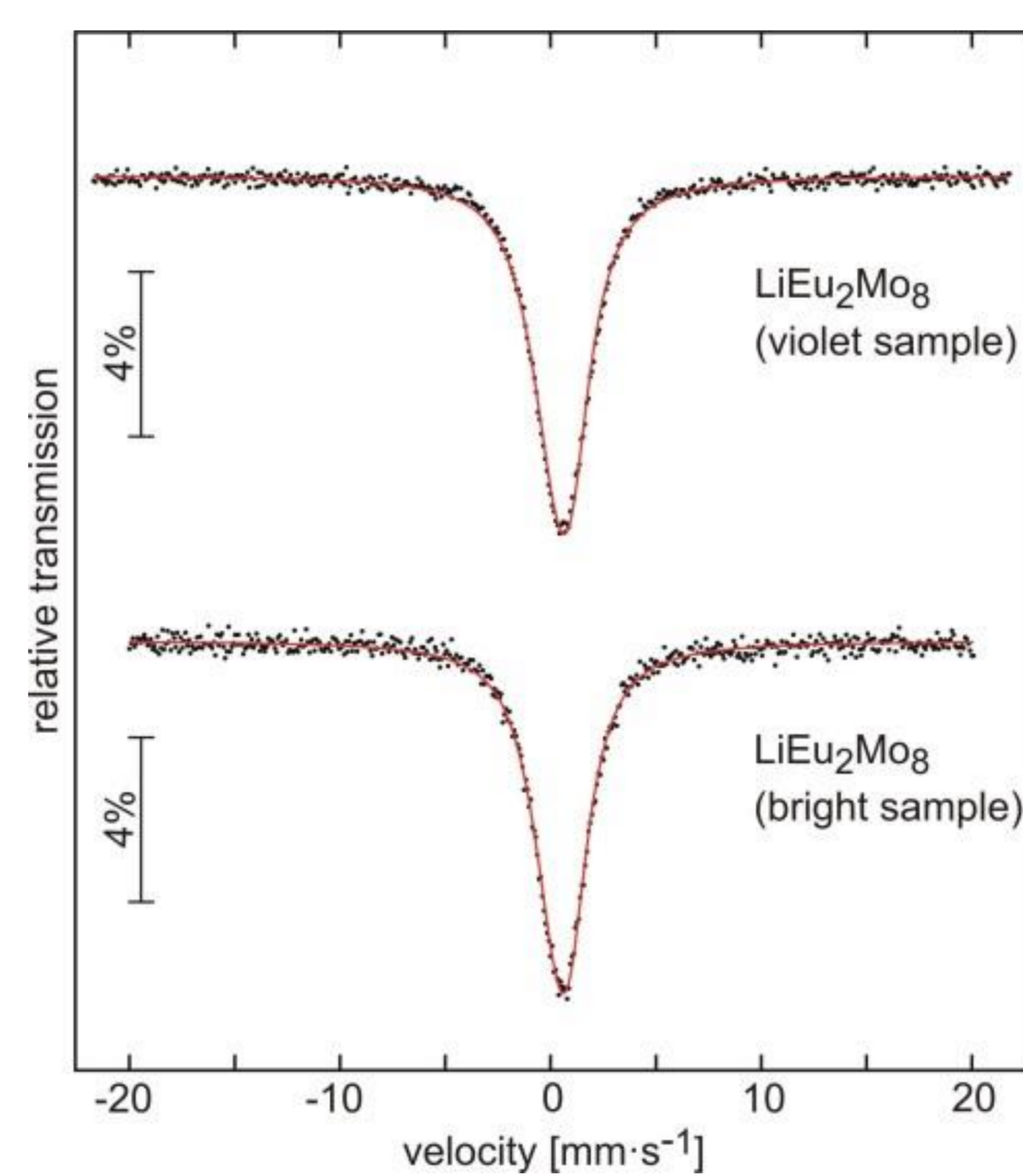
**Fig. 1** . LEM crystal fragments of violet LEM (left) and shiny LEM (right) at ambient light (top) and upon excitation at 365 nm (bottom).

## Pure trivalent Europium

In contrast to the different absorption behavior in the visible, both crystal shades show exactly the same emission spectra for the  $^5\text{D}_0-^7\text{F}_J$  ( $J = 0$  to 4) emission of  $\text{Eu}^{3+}$ , which indicate the same chemical surrounding of the trivalent europium ions (Fig. 2). Furthermore the  $^{151}\text{Eu}$  Mössbauer spectra of the bright and also of the dark violet  $\text{LiEuMo}_2\text{O}_8$  samples show the presence trivalent europium solely (Fig. 3). Therefrom is apparent that the differences in the crystals do not occur by the activator ion.



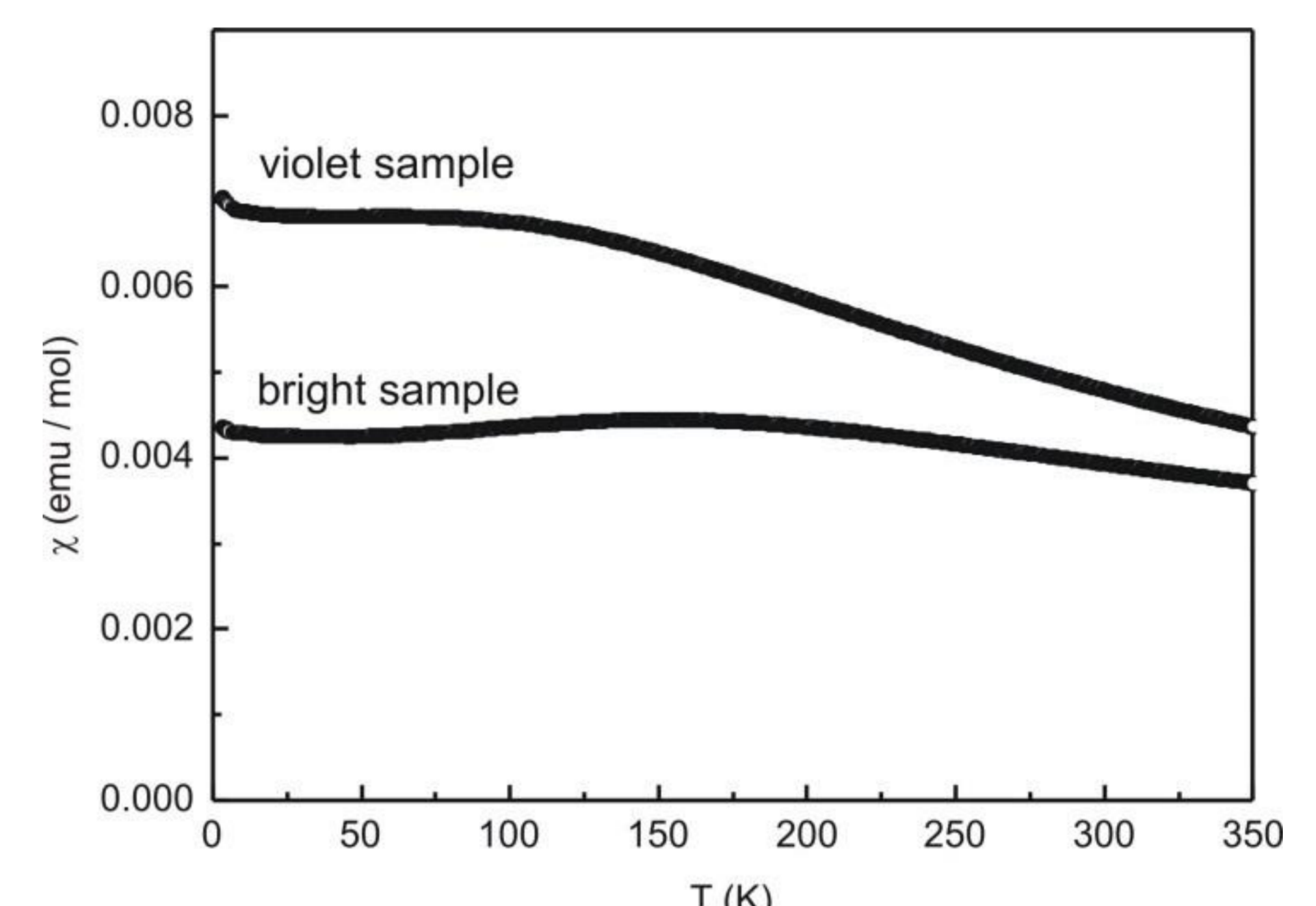
**Fig. 2** Normalized emission spectra of a bright and a dark violet sample of  $\text{LiEuMo}_2\text{O}_8$  at room temperature.



**Fig. 3** Experimental and simulated (red lines)  $^{151}\text{Eu}$  Mössbauer spectra of bright and violet  $\text{LiEuMo}_2\text{O}_8$  sample at room temperature

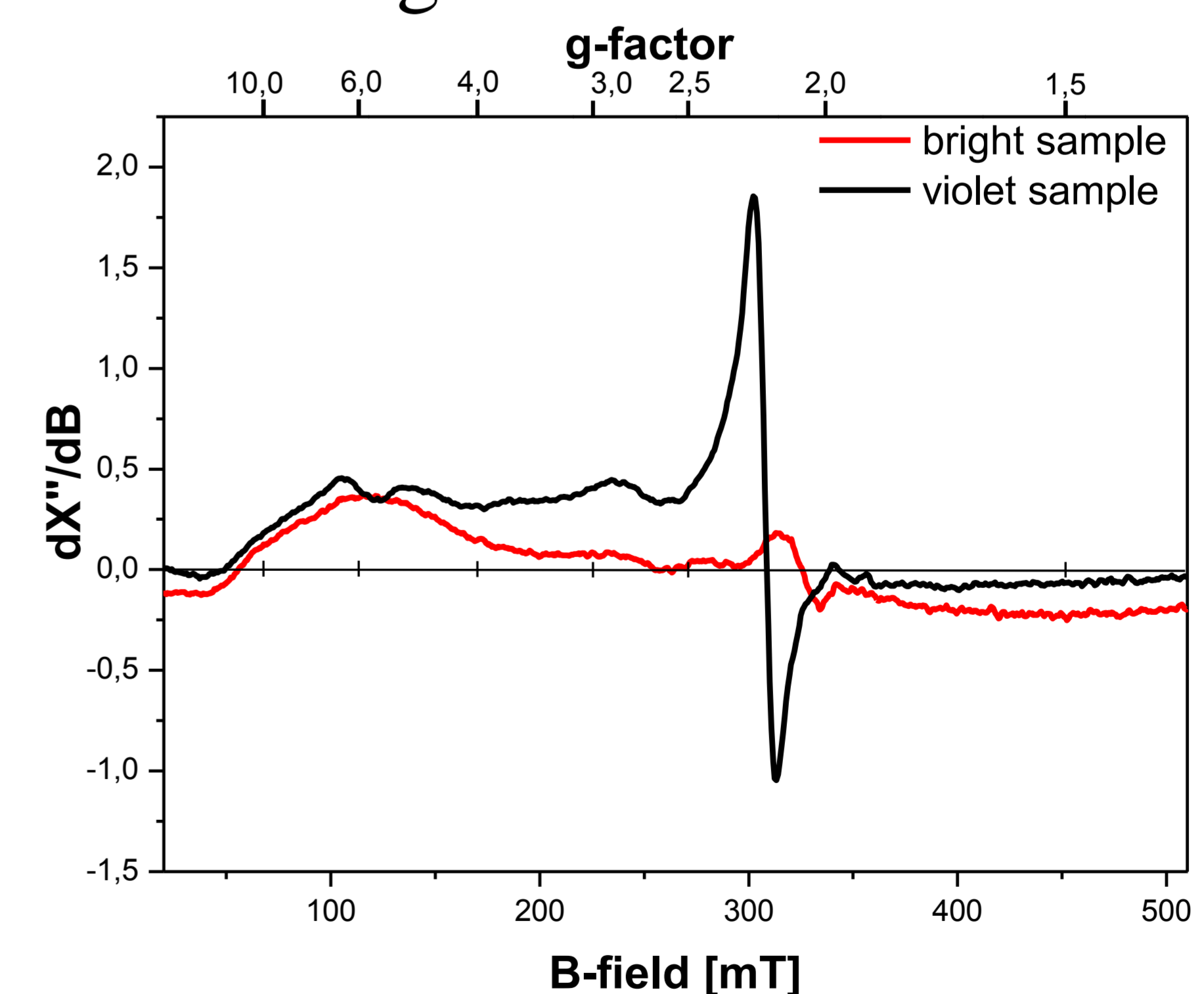
## The Tribute of $\text{Mo}^{5+}$

The first hint to molybdenum as origin for the dark violet  $\text{LiEuMo}_2\text{O}_8$  was given by temperature dependent magnetic susceptibility data (Fig. 4) which indicate an another component in addition to the weak van Vleck type paramagnetism of trivalent europium ( $[\text{Xe}]4f^6$ ) in the violet sample.



**Fig. 3** Temperature dependence of the magnetic susceptibility of a bright and a dark violet sample of  $\text{LiEuMo}_2\text{O}_8$  measured at 10 kOe.

Electron spin resonance measurements were able to prove the hypothesis of defects in the oxygen substructure accompanied by partial reduction of  $\text{Mo}^{6+}$  ( $d^0$ ) to  $\text{Mo}^{5+}$  ( $d^1$ ) (Fig.5) detectable at  $g = 2.2$



**Fig. 5** X-band cw-EPR spectra of a bright and dark violet sample of  $\text{LiEuMo}_2\text{O}_8$  at room temperature.

## Conclusion

The concentration of pentavalent molybdenum is too low to be monitored by x-ray analysis but large enough to have a significant influence on the physical properties of the material. This can be explained by the incorporation of molybdenum(V) ions ( $[\text{Kr}]4d^1$ ) as a result of the reduction of the molybdate units, which implies the formation of oxygen vacancies for charge compensation as well.