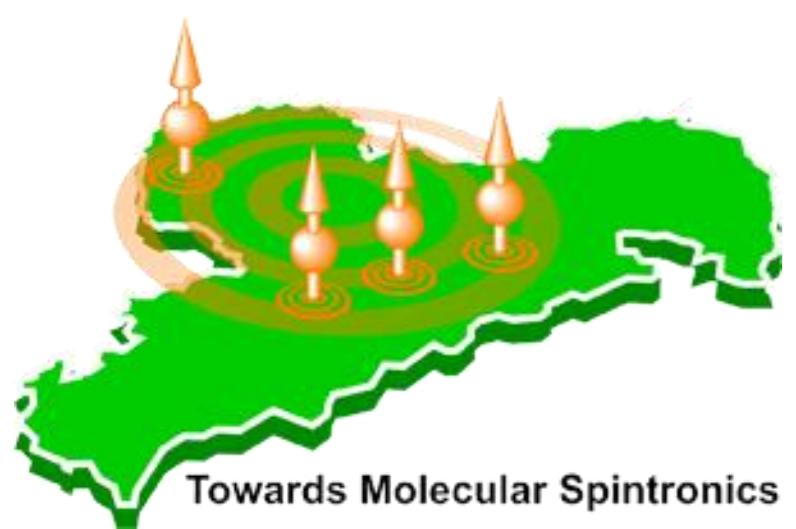


SP2 + SP4 : $[\text{Ni}_2(\text{O}_2\text{CH})_4(\text{tmada})_2(\text{H}_2\text{O})]$ - Synthesis, Characterization, ESR and Magnetic Studies



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Synthesis and characterization of $[\text{Ni}_2(\text{O}_2\text{CH})_4(\text{tmada})_2(\text{H}_2\text{O})]$

The synthesis of several water-bridged nickel dimers with the general formula $[\text{Ni}_2(\text{O}_2\text{CR})_4(\text{N}\cap\text{N})_2(\text{H}_2\text{O})]$ ($\text{N}\cap\text{N}$ = amine; R = organic residue) is already described in the literature [1 – 3]. Thereby, two of the carboxylato ligands are coordinated monodentate to each Ni atom and the remaining ligands act in a μ -bridging fashion.

For selected $[\text{Ni}_2(\text{O}_2\text{CR})_4(\text{N}\cap\text{N})_2(\text{H}_2\text{O})]$ type complexes ($\text{N}\cap\text{N}$ = *N,N,N',N'*-tetramethylethylene-diamine, tmada; R = CH_3 , CH_2Cl , Et, CF_3 , CHClCH_3 , $(\text{CH}_2)_2\text{Cl}$) Turpeinen *et al.* reported weak antiferromagnetic interactions (Curie-Weiss temperature of ca. 1 – 6 K) and in some cases these interactions are so weak that no maximum of the magnetic susceptibility are observed above 2 K ($\chi_{\text{max}} = 2$ – 4 K). In contrast, Eremenko *et al.* reported for $[\text{Ni}_2(\text{O}_2\text{CMe}_3)_4(\text{py})_4(\text{H}_2\text{O})]$ intramolecular ferromagnetic together with intermolecular antiferromagnetic interactions with an effective magnetic moment (per nickel atom) of $2.61 \mu\text{B}$ (5 K) [2].

This motivated us to investigate the magnetic properties of perhaps the most simple $[\text{Ni}_2(\text{O}_2\text{CR})_4(\text{N}\cap\text{N})_2(\text{H}_2\text{O})]$ type complex, namely of $[\text{Ni}_2(\text{O}_2\text{CH})_4(\text{tmada})_2(\text{H}_2\text{O})]$ (1).

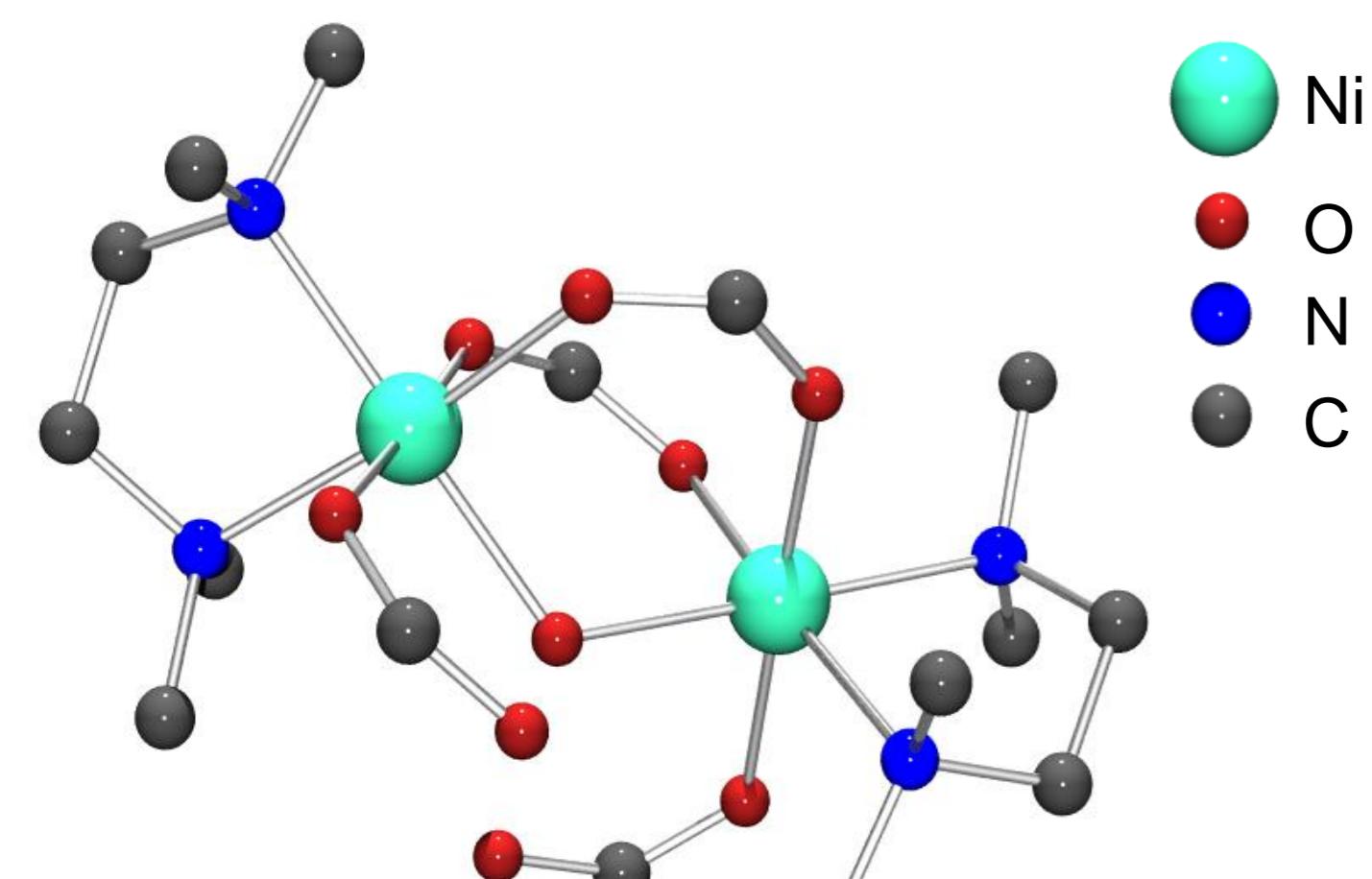


Fig. 1. Structure of $[\text{Ni}_2(\text{O}_2\text{CH})_4(\text{tmada})_2(\text{H}_2\text{O})]$ (1) in the solid state.

Single crystals were obtained by slow evaporation of an acetone solution containing 1 at room temperature. The dimeric complex crystallizes in the monoclinic space group $\text{C}2/\text{c}$ within two octahedrally distorted Ni(II) ions.

There are two binding modes of the formato groups in 1 (terminal monodentate and bridged bidentate) and hence a splitting of the asymmetric and symmetric C–O valence vibration in the IR with two different $\Delta\nu$ should be expected [5]. The obtained spectrum shows only one set of the symmetric carboxylate vibration. The obtained $\Delta\nu$ reflects the different binding modes of the formato group.

$\Delta\nu_1 = 281 \text{ cm}^{-1} \rightarrow$ monodentate formato group
 $\Delta\nu_2 = 196 \text{ cm}^{-1} \rightarrow$ bridging formato group

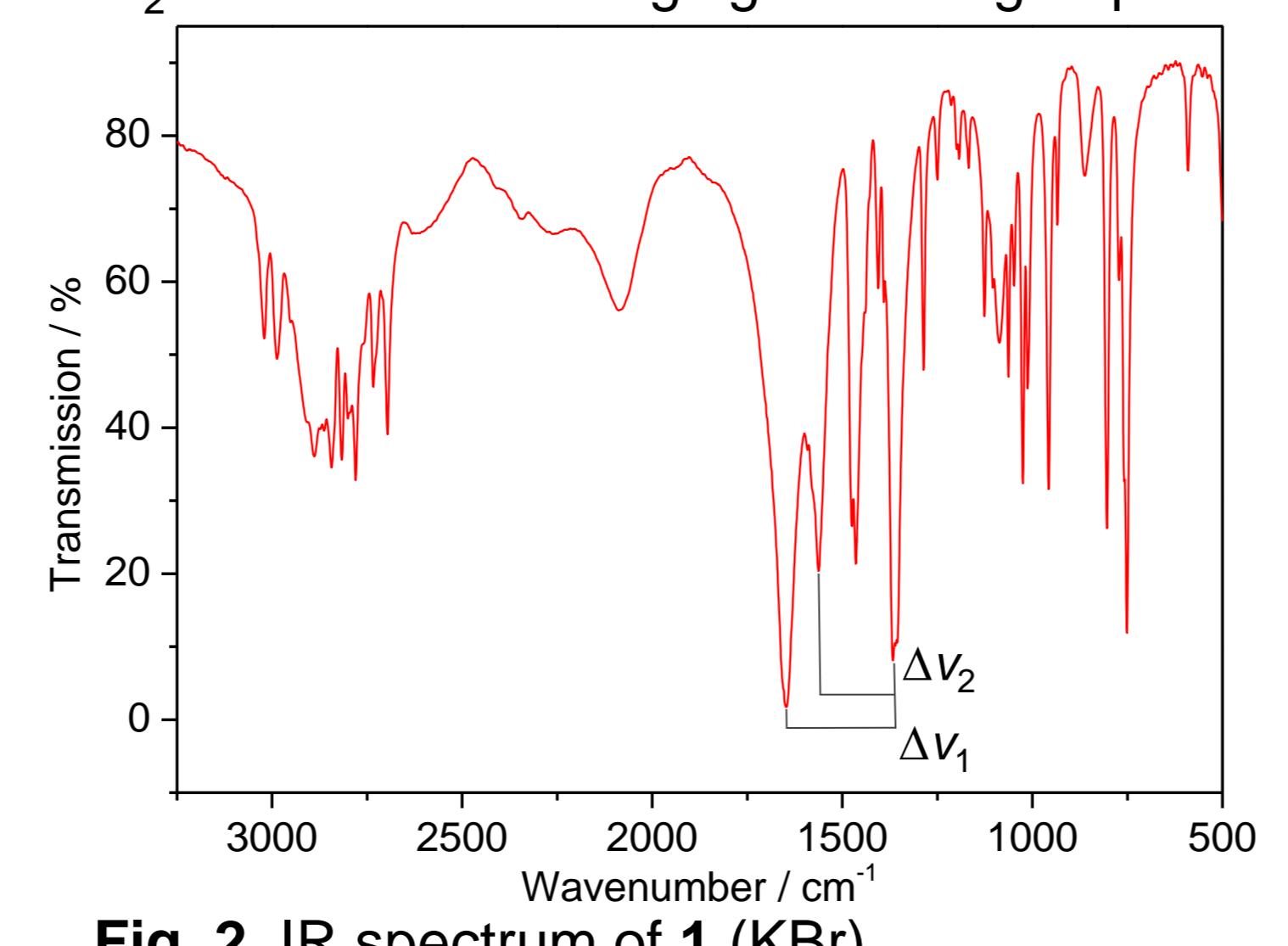
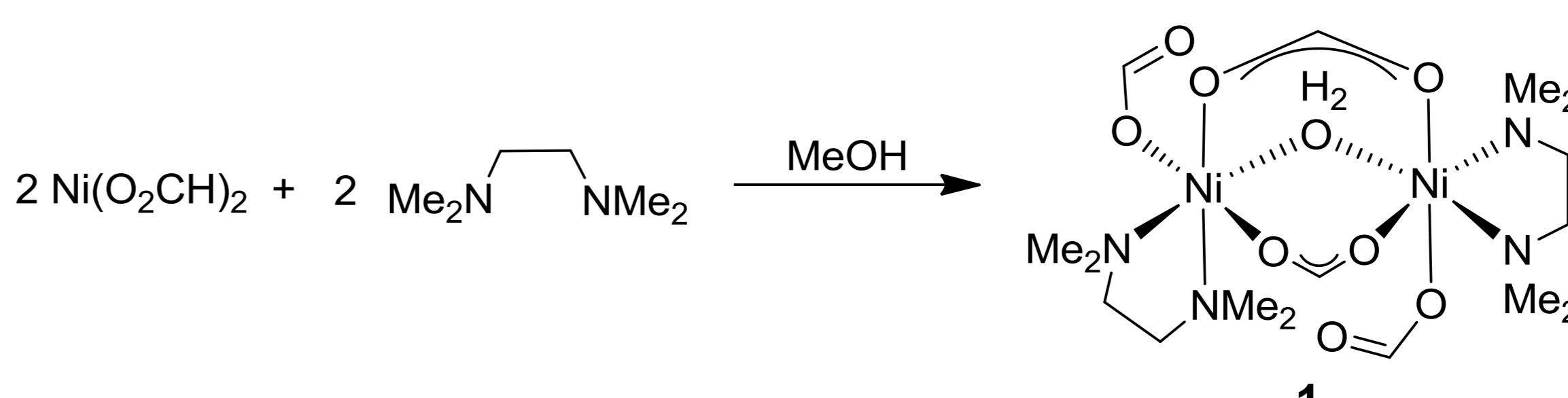


Fig. 2. IR spectrum of 1 (KBr).

1 was prepared by addition of tmada to a solution of $[\text{Ni}(\text{O}_2\text{CH})_2]$ in methanol with stirring for 24 h. After filtration, the solution was evaporated to dryness and recrystallized from acetone [4].



Synthesis of Ni(II) dimer 1.

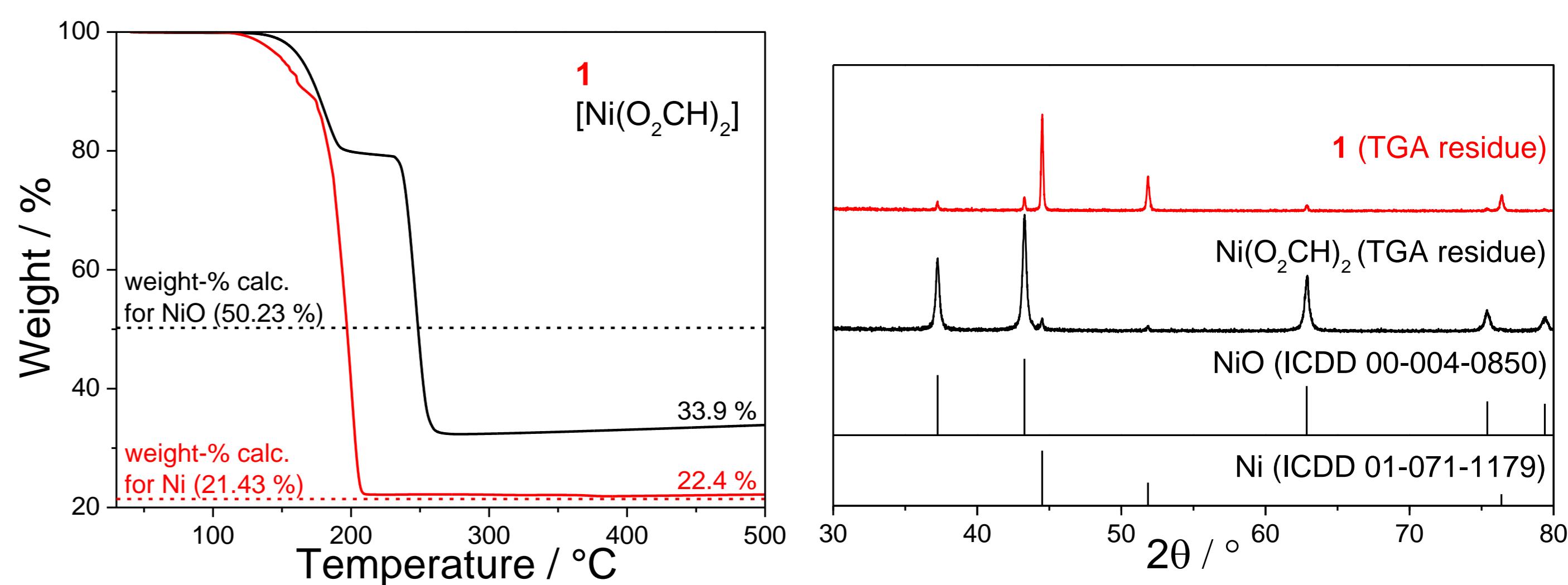


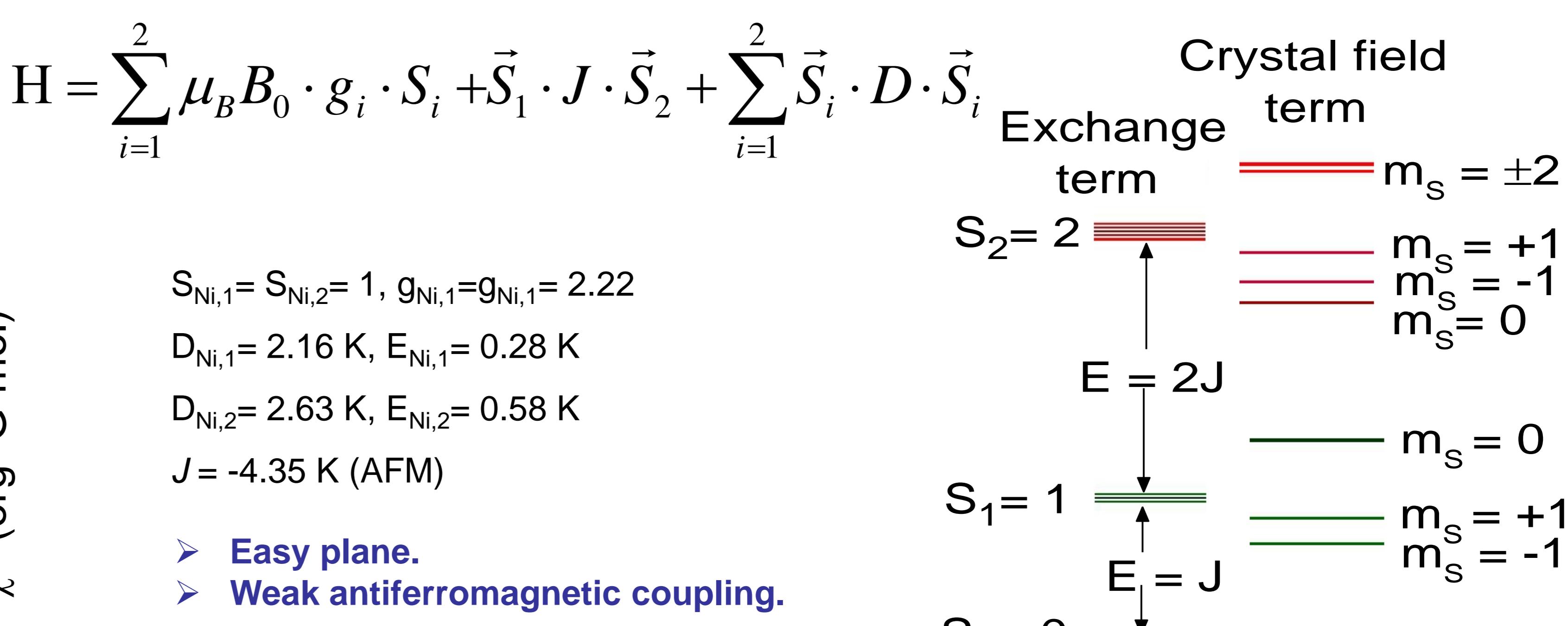
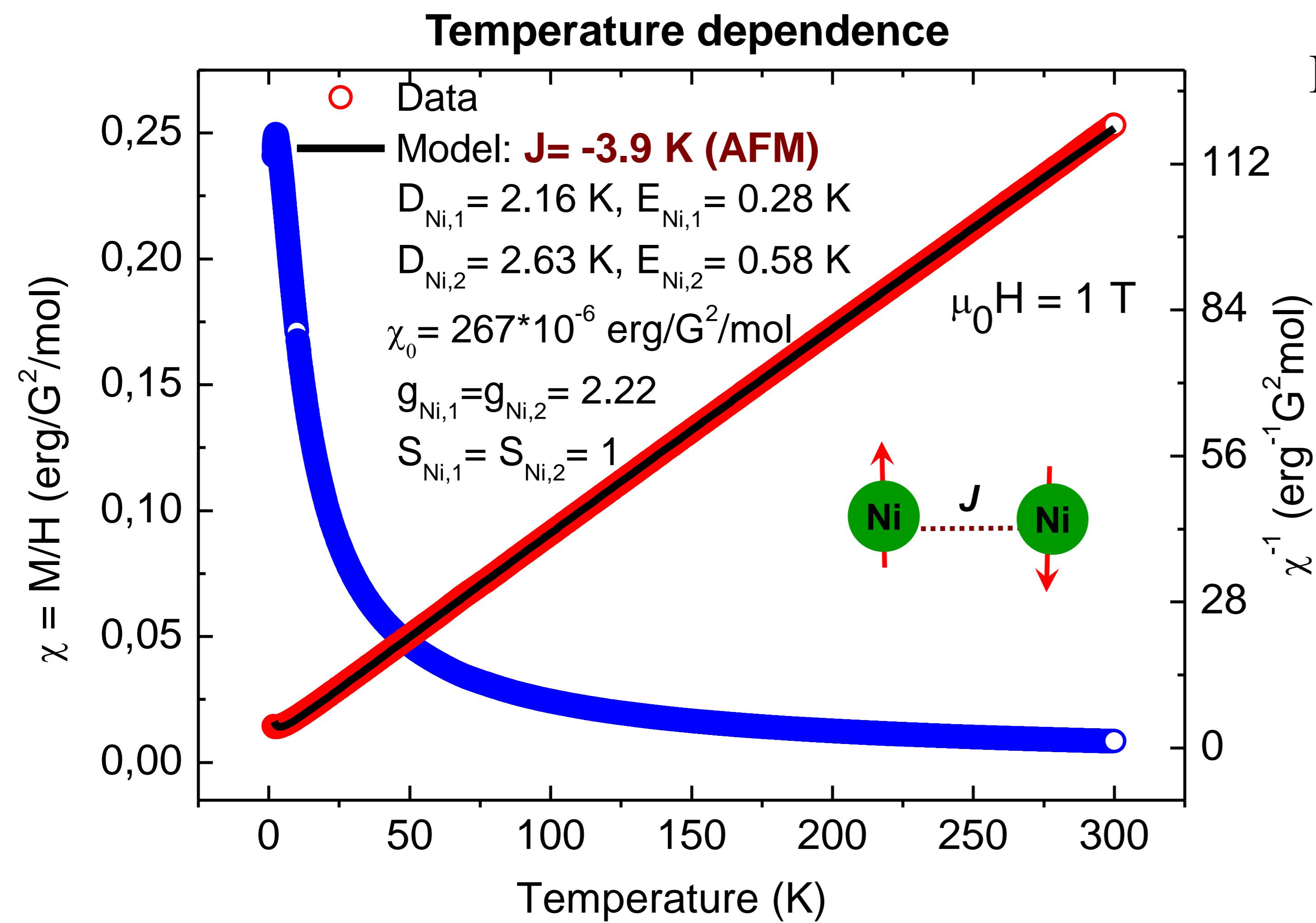
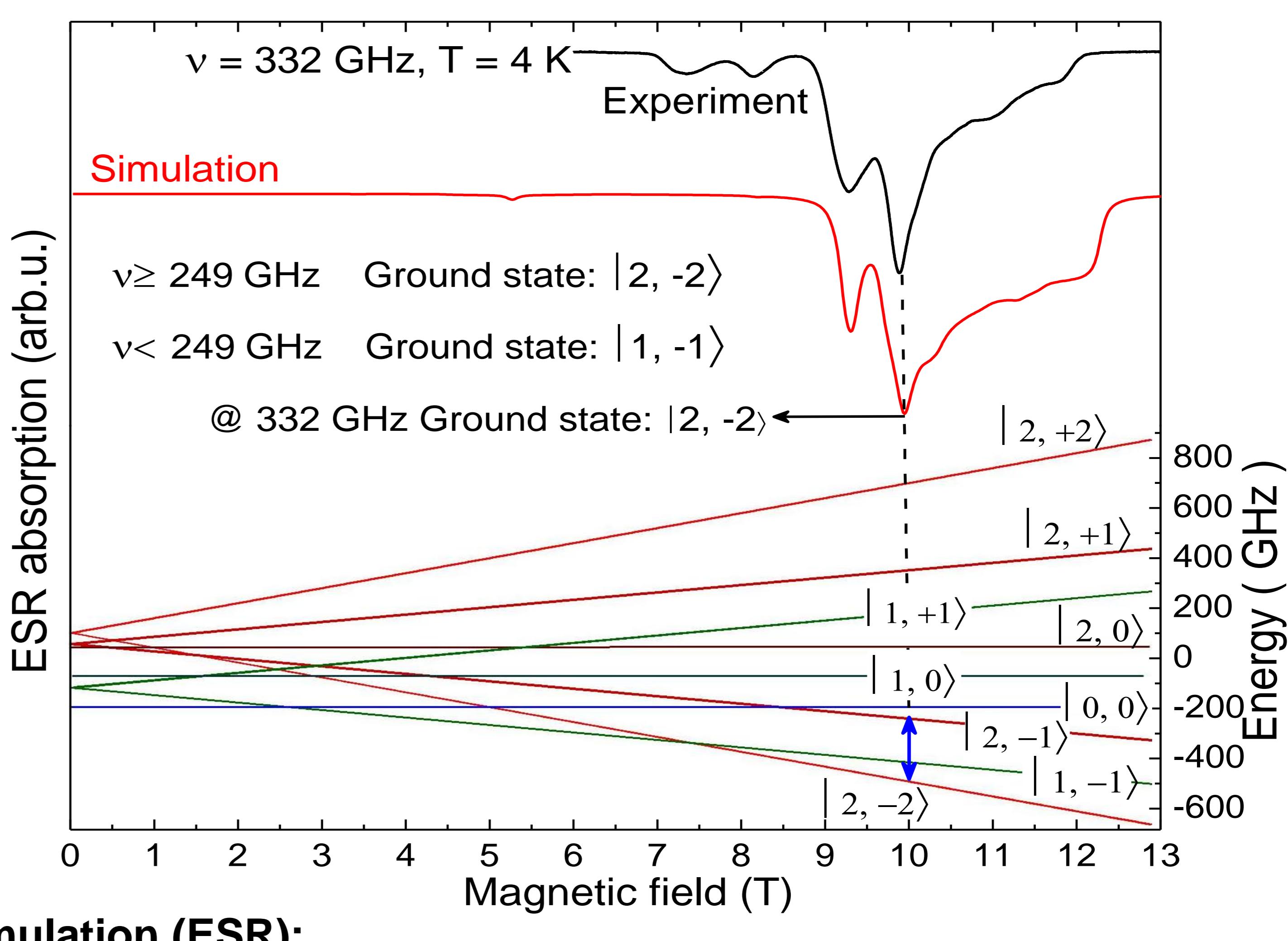
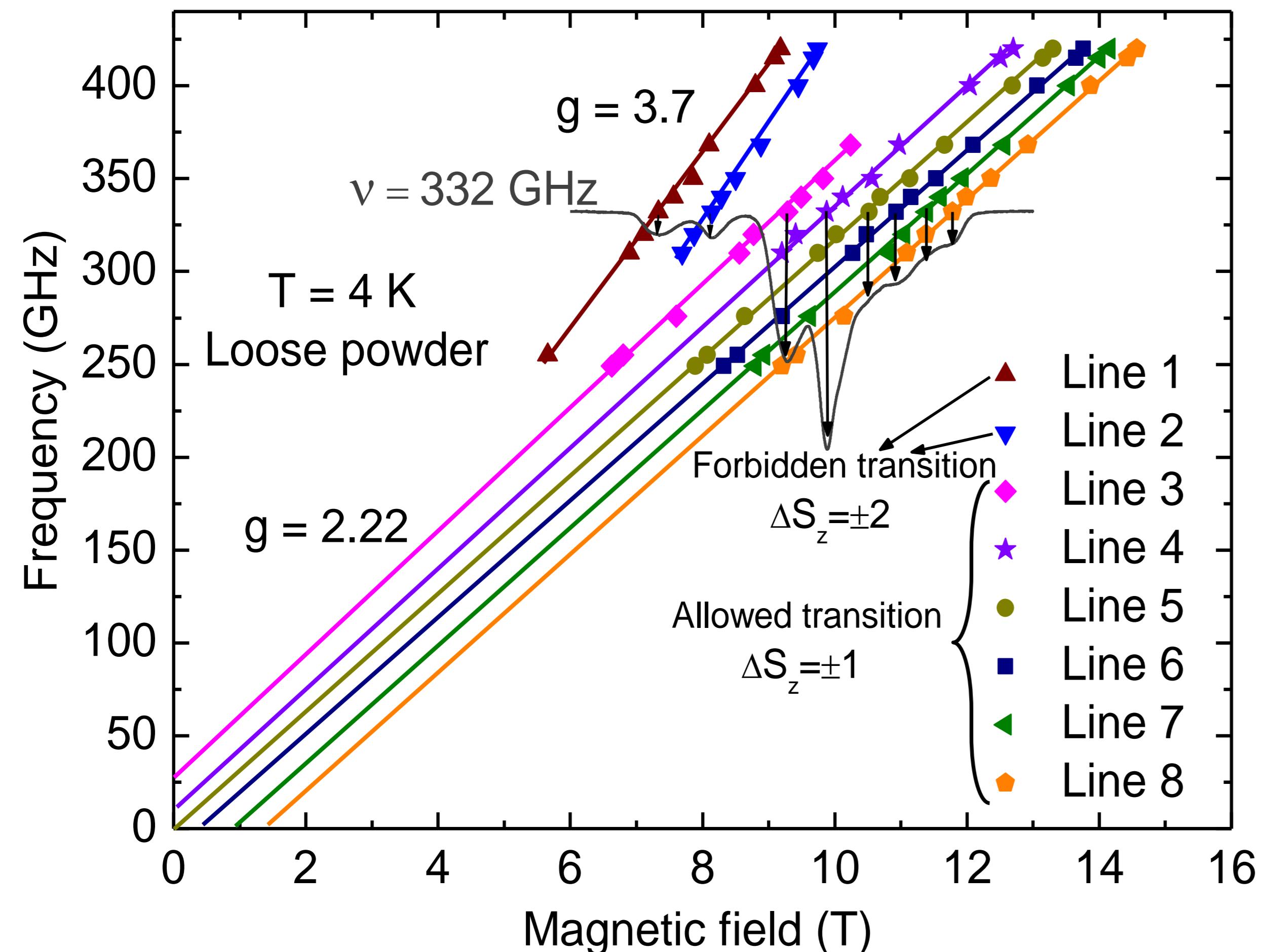
Fig. 3. TG traces of 1 (40–500 °C, 10 K/min, 60 mL/min N_2) and Ni(II) formate (40–500 °C, 5 K/min, 60 mL/min Ar) (left). XRPD pattern of the residues of the TG studies (right).

As shown in Fig. 3 complex 1 and Ni(II)-formate decompose thermally in two steps. The second decomposition step occurs at a higher temperature for Ni(II)-formate than for 1.

The XRPD of the TGA residue of 1 displays most predominantly the typical reflections of Ni as well as traces of NiO. In contrast, for the TGA residue of $[\text{Ni}(\text{O}_2\text{CH})_2]$ the opposite has been observed. The discrepancy between calculated and observed weight loss of $[\text{Ni}(\text{O}_2\text{CH})_2]$ might be due to a sublimation process.

High-Field ESR & magnetization studies

Frequency vs. resonance field ν (Hres)-dependencies of the ESR resonance modes



References & Acknowledgement

[1] U. Turpeinen *et al.* *Polyhedron*, 1987, 6, 1603–1610. [2] Eremenko *et al.* *Russ. Chem. Bull.* 1998, 47, 704–718. [3] A. Karmakar *et al.* *Eur. J. Inorg. Chem.* 2006, 4673–678. [4] A. Abylaikhan, *Dissertation*, TU Chemnitz 2005. [5] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds Part B*, 6th Edition, Wiley, New Jersey, 2009.

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