

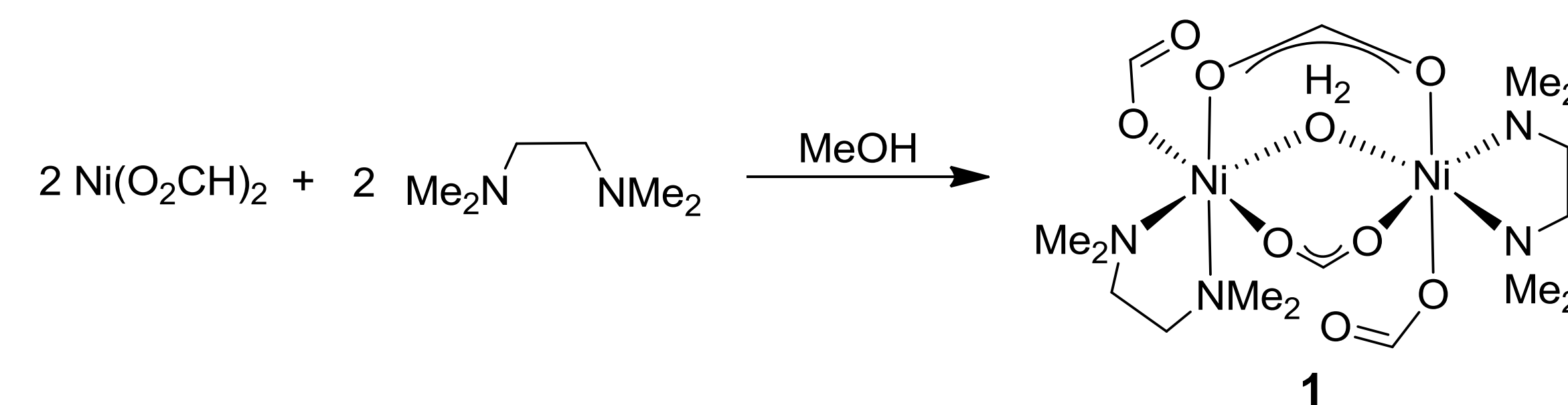
## Synthesis and characterization of $[\text{Ni}_2(\text{O}_2\text{CH})_4(\text{tmeda})_2(\text{H}_2\text{O})]$

The synthesis of several water-bridged nickel dimers with the general formula  $[\text{Ni}_2(\text{O}_2\text{CR})_4(\text{N}\text{N})_2(\text{H}_2\text{O})]$  ( $\text{N}\text{N}$  = amine;  $\text{R}$  = 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  $\mu$ -bridging fashion.

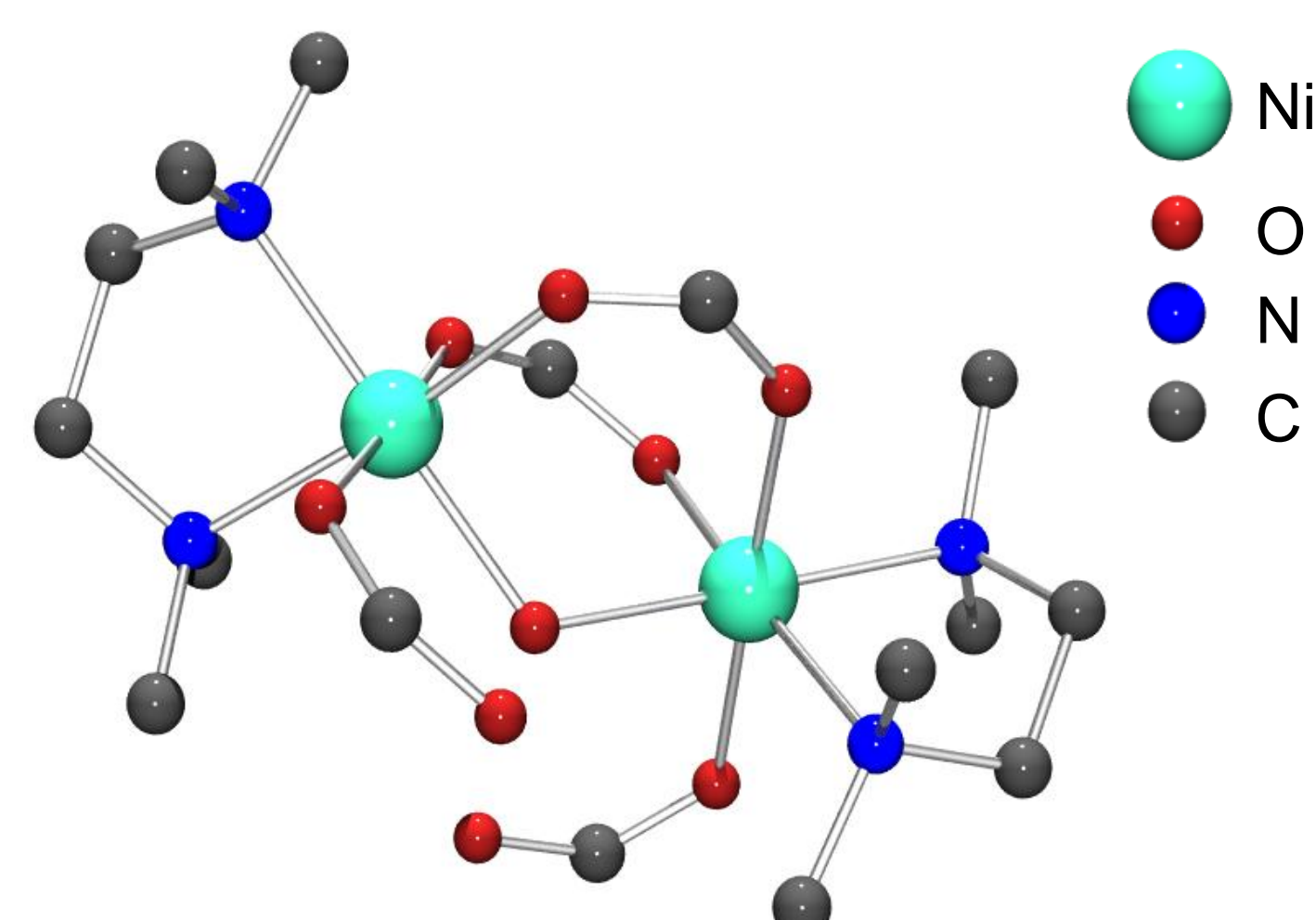
For selected  $[\text{Ni}_2(\text{O}_2\text{CR})_4(\text{N}\text{N})_2(\text{H}_2\text{O})]$  type complexes ( $\text{N}\text{N}$  =  $N,N,N',N'$ -tetramethylethylenediamine, tmeda;  $\text{R}$  =  $\text{CH}_3$ ,  $\text{CH}_2\text{Cl}$ , Et,  $\text{CF}_3$ ,  $\text{CHClCH}_3$ ,  $(\text{CH}_2)_2\text{Cl}$ ) 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  $\mu_B$  (5K) [2].

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

**1** was prepared by addition of tmeda 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**.

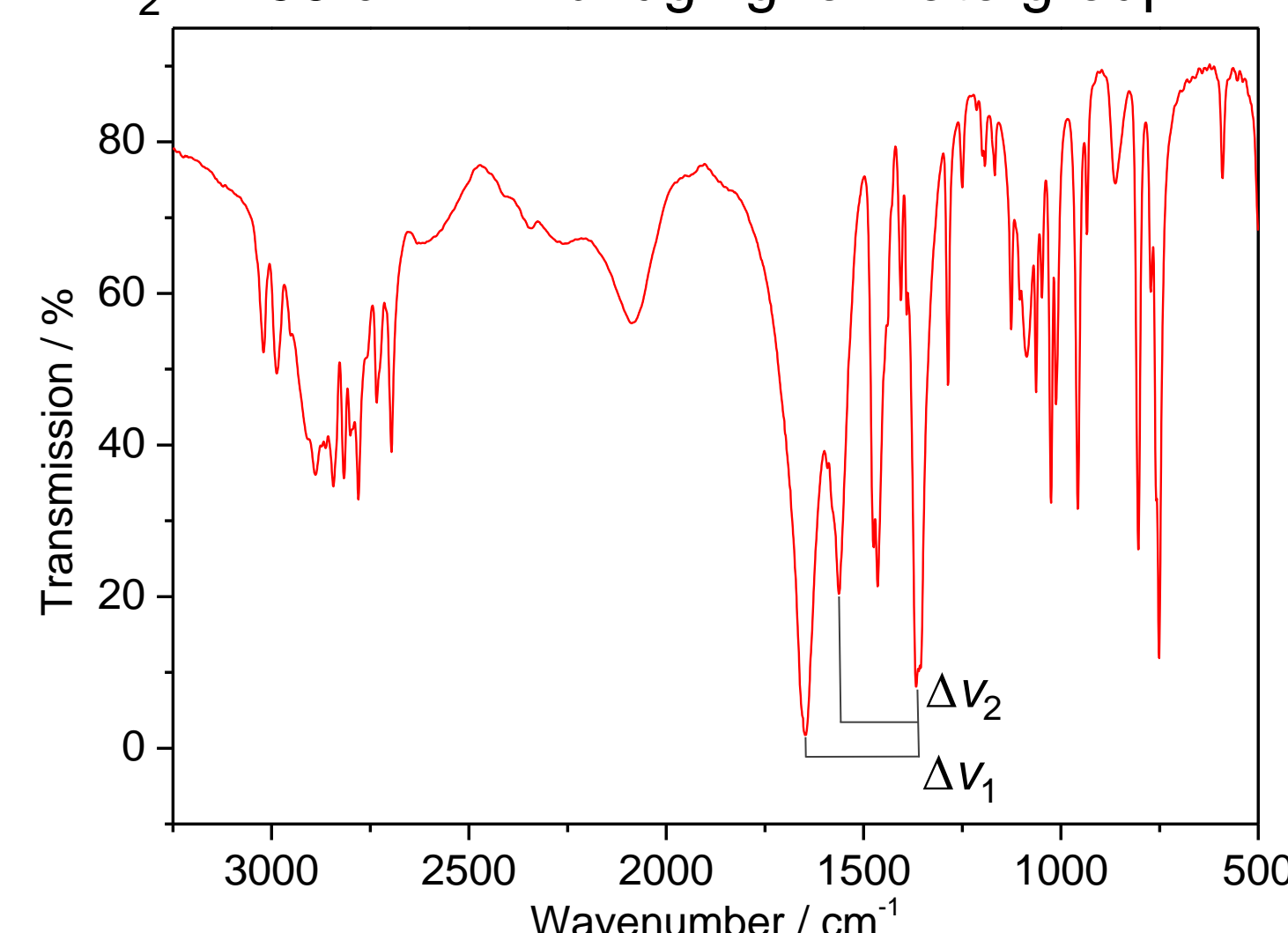


**Fig. 1.** Structure of  $[\text{Ni}_2(\text{O}_2\text{CH})_4(\text{tmeda})_2(\text{H}_2\text{O})]$  (**1**) in the solid state.

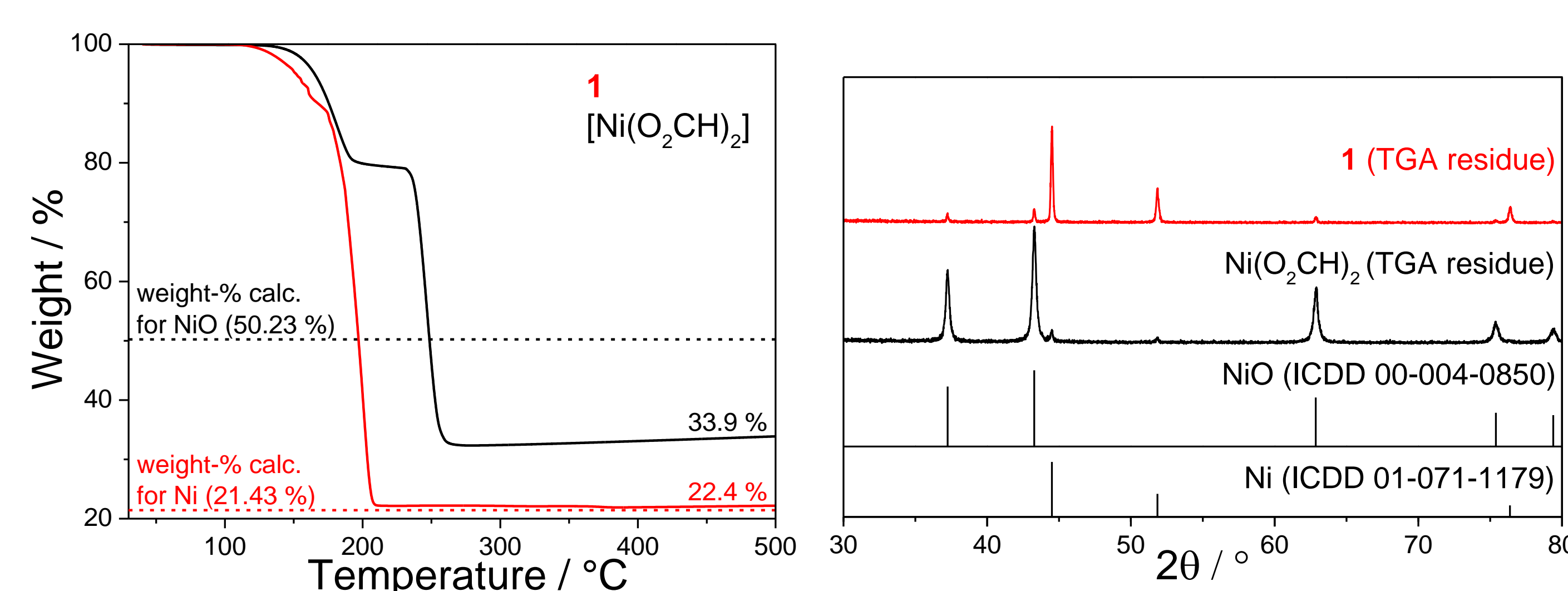
Single crystals were obtained by slow evaporation of an acetone solution containing **1** at room temperature. The dimeric complex crystallizes in the monoclinic space group  $C2/c$  within two octahedrally distorted Ni(II) ions.

There are two binding modes of the formate 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 formate group.

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



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



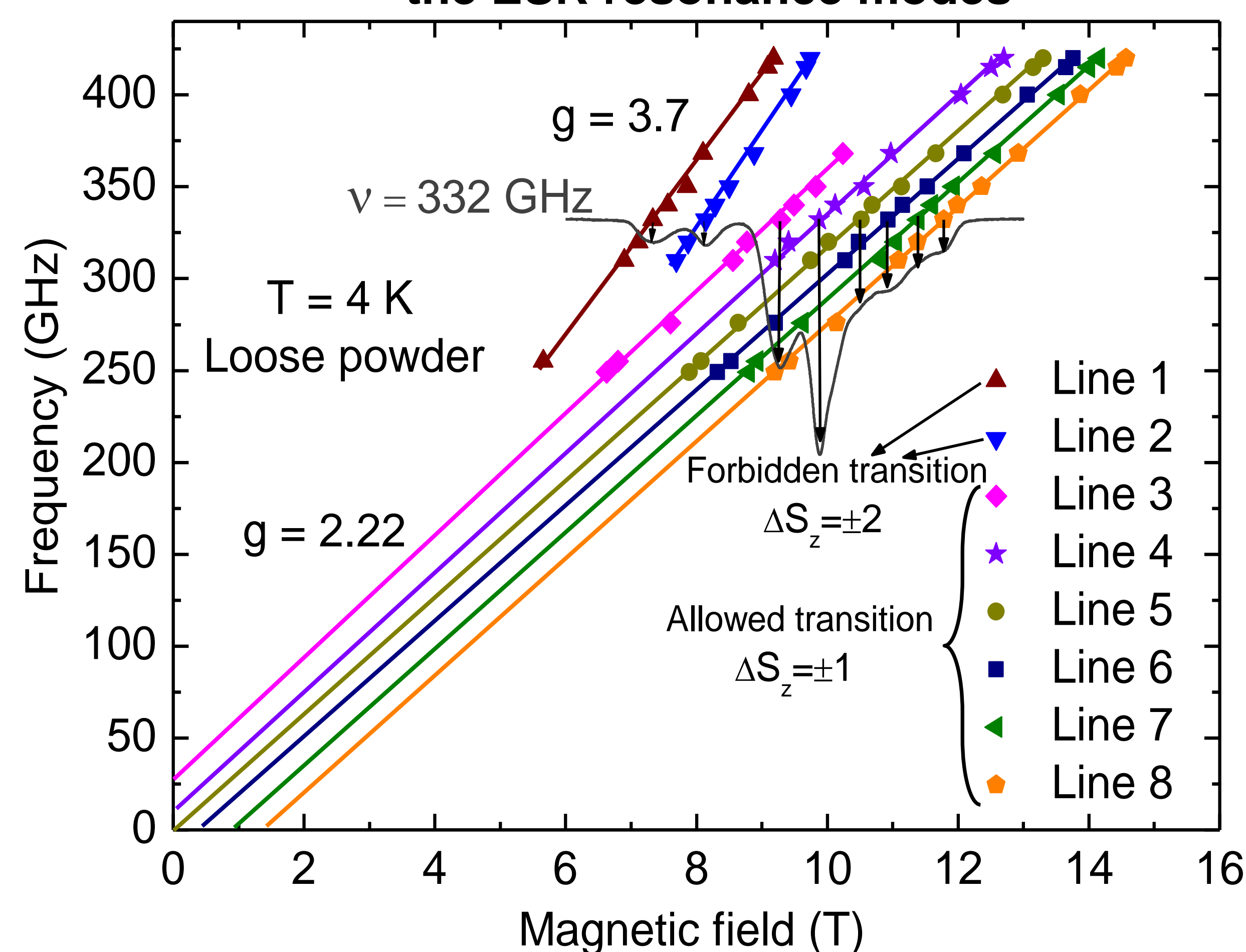
**Fig. 3.** TG traces of **1** (40–500 °C, 10 K/min, 60 mL/min  $\text{N}_2$ ) and Ni(II) formate (40–500 °C, 5 K/min, 60 mL/min Ar) (left). XRPD pattern of the residues of the TG studies (right).

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**.

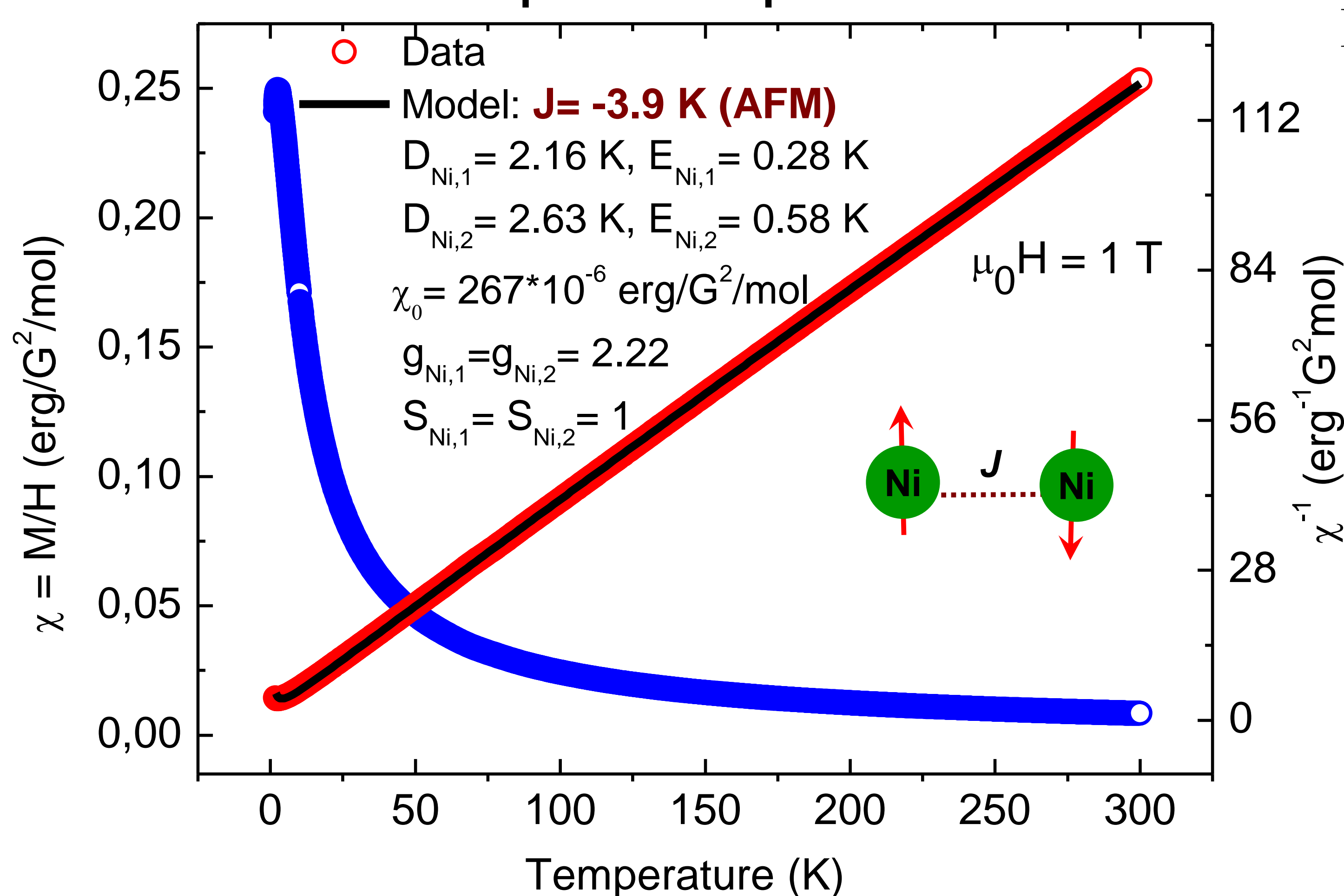
The XRPD of the TGA residue of **1** displays most predominantly the typical reflections of Ni as well as traces of NiO. In contrast, for the TGA residue of  $[\text{Ni}(\text{O}_2\text{CH})_2]$  the opposite has been observed. The discrepancy between calculated and observed weight loss of  $[\text{Ni}(\text{O}_2\text{CH})_2]$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

## High-Field ESR & magnetization studies

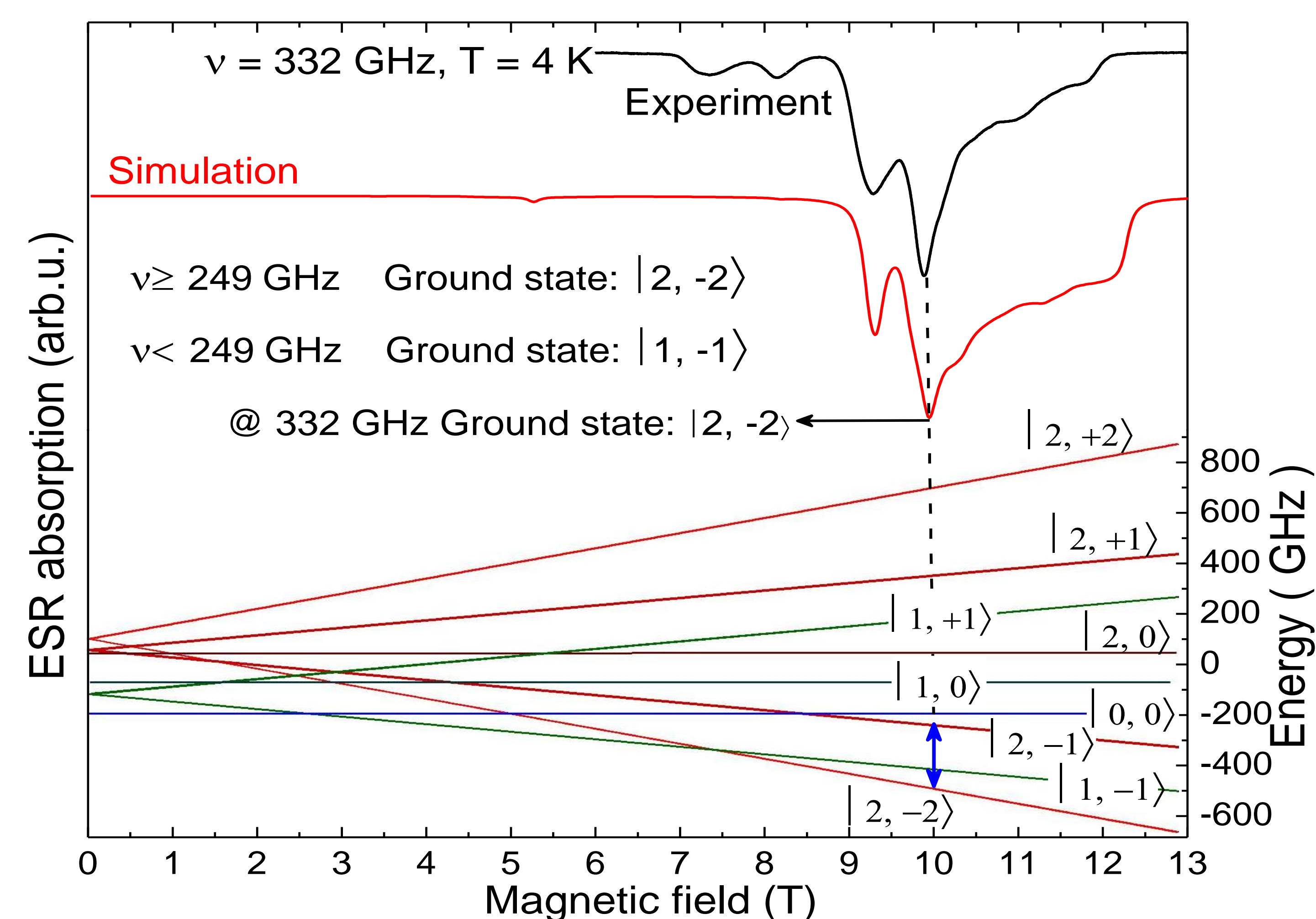
### Frequency vs. resonance field $\nu(\text{Hres})$ -dependencies of the ESR resonance modes



### Temperature dependence



➤ **Weak antiferromagnetic coupling between Ni spins.**



### Simulation (ESR):

$$H = \sum_{i=1}^2 \mu_B B_0 \cdot g_i \cdot S_i + \vec{S}_1 \cdot J \cdot \vec{S}_2 + \sum_{i=1}^2 \vec{S}_i \cdot D \cdot \vec{S}_i$$

Crystal field term

Exchange term

$S_2 = 2$

$E = 2J$

$S_1 = 1$

$E = J$

$S_0 = 0$

Energy levels:  $m_s = \pm 2$ ,  $m_s = +1$ ,  $m_s = -1$ ,  $m_s = 0$

Parameters:  $S_{\text{Ni},1} = S_{\text{Ni},2} = 1$ ,  $g_{\text{Ni},1} = g_{\text{Ni},2} = 2.22$ ;  $D_{\text{Ni},1} = 2.16 \text{ K}$ ,  $E_{\text{Ni},1} = 0.28 \text{ K}$ ;  $D_{\text{Ni},2} = 2.63 \text{ K}$ ,  $E_{\text{Ni},2} = 0.58 \text{ K}$ ;  $J = -4.35 \text{ K (AFM)}$

➤ **Easy plane.**  
➤ **Weak antiferromagnetic coupling.**

## 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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