Phys Chem Minerals (2004) 31: 190–193
DOI 10.1007/s00269-004-0381-3

ORIGINAL PAPER

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Characterisation of the antiferromagnetic transition of Cu_2FeSnS_4, the synthetic analogue of stannite

Received: 5 September 2003 / Accepted: 2 January 2004

Abstract Magnetisation measurements were performed on the synthetic analogue of stannite, Cu_2FeSnS_4, in order to characterise the antiferromagnetic transition at low temperature, evidenced by Bernardini et al. (2000). Temperature and field dependence of the material were checked by means of static magnetisation measurements, carried out scanning the magnetic fields up to 12 T and temperatures in the range 1.4–20 K, while *ac* susceptibility data were collected at different frequencies ranging from 1.8 to 510 Hz. Both static and dynamic magnetisation data, performed above and below the Néel temperature, 6.1(2) K, confirm stannite to order antiferromagnetically at a long-range scale. Moreover, an increase of both the magnetic anisotropy and the exchange interaction, with respect to the Mn-analogue (Fries et al. 1997), has been observed.

Keywords Stannite · Antiferromagnetism · *ac* susceptibility · Néel temperature

Introduction

Quaternary I_2–II–IV–VI_4 chalcogenides (II = Fe, Mn, Co), having structures derivatives of either sphalerite or wurtzite, have been proposed as a successful way to control both the metal distribution and the metal–metal distance, thus reaching peculiar magnetic properties, usually different from those of the archetype structured materials (Kreissl and Gehlhoff 1984; Furdyna 1988; Fries et al. 1997; Babic Stojic et al. 1999; Feltin et al. 1999). The ordered cation distribution of these materials, in fact, accompanied by the decrease of the symmetry from cubic to tetragonal and from hexagonal to orthorhombic, is mainly driven by the minimisation of the mismatch, induced by the large IV cations, determining the paramagnetic substituents to occur at distances larger than $\sim$ 5.5 Å (in spite of $\sim$ 3.8 Å in sphalerite/wurtzite).

Stannite, Cu_2FeSnS_4, one of the most studied sulfide minerals owing to its economic importance as an Sn ore and to its semiconducting properties, crystallises in the $I\bar{4}2m$ space group (Fig. 1; Hall et al. 1978; Bernardini et al. 1990, 2000). The lattice constants of the pure synthetic analogue, a and c, have been refined to 5.450 and 10.726 Å, respectively (Bernardini et al. 1990, 2000). Three different tetrahedral sites may be distinguished and the Fe positions (0,0,0) form a tetragonal body-centred lattice, where the lowest Fe–Fe distances are a and $1/2\sqrt{2a^2 + c^2}$, respectively (Hall et al. 1978; Bernardini et al. 1990). Eibschütz et al. (1967), by means of high-temperature magnetic and Mössbauer measurements, proved the valence states of the cations to be Cu(I), Fe(II) and Sn(IV). Bernardini et al. (2000), while refining the characterisation of Cu valence state using EPR spectroscopy, observed the presence of a transition in the low-temperature regime, with an antiferromagnetic character ($T_N \sim 8$ K). Apart from the correlation between the tetrahedral coordination and the antiferromagnetic nature of the interaction, which characterises most of the Fe(II)-bearing sulfides (Vaughan and Burns 1972), no further investigations have been undertaken. Recently, an extensive characterisation of the magnetic properties of the Mn analogue of stannite, Cu_2MnSnS_4 (Fries et al. 1997; McCabe et al. 1997), proved the low-temperature magnetisation measurements, with constant and variable applied fields, to be a unique tool to study the behaviour of the magnetic ordering of such materials below the Néel temperature. This research, therefore, has been fostered to refine and extend the available data about the magnetic transition in stannite.

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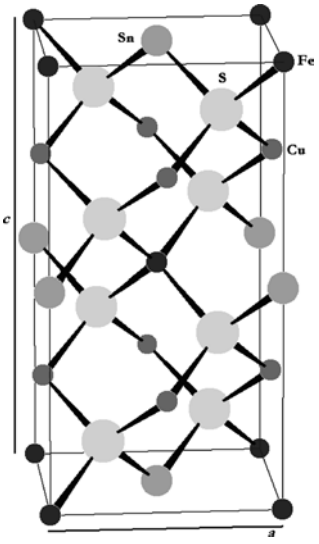

Fig. 1 Crystal structure of stannite

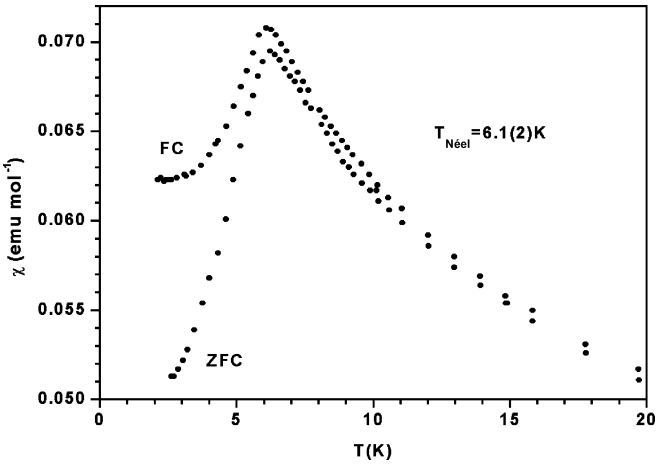

Fig. 2 ZFC/FC (emu mol^{-1}) susceptibility vs. T(K) curves; applied field: 0.008 T

Experimental

The procedure for the synthesis of the pure Cu_2FeSnS_4 analogue of stannite has been described elsewhere (Bernardini et al. 1990, 2000). A small amount of the material prepared and characterised by Bernardini et al. (2000) was selected and ground for the new experimental investigations. These authors confirmed the stoichiometry of the sample by means of EPMA analyses, while only tetragonal stannite and traces of herzenbergite (SnS) were observed in X-ray powder pattern. This latter phase is probably a residue of the intermediate step of reaction. The presence of herzenbergite has not been considered relevant to the investigation of the magnetic properties, because of its complete diamagnetism.

Magnetisation measurements at low magnetic fields (applied field H = 0.008 T) were performed with Cryogenic S600 Superconducting QUantum Interference Device (SQUID) magnetometer. Corrections for molecular diamagnetism, estimated from Pascal's constants (O'Connor 1982), were applied. Zero-field-cooled/field-cooled static susceptibility data were obtained in the range 1.4–20 K, above and below the observed Néel temperature, with a temperature step of approximately 0.2 K. In the same temperature range, *ac* susceptibility measurements were performed at different frequencies, ω, ranging from 1.81 to 510 Hz. Magnetisation data with applied fields up to 12 T were obtained, at 1.4 and 1.9 K, by using a highly sensitive vibrating sample magnetometer (Oxford Instruments), the increment step being 0.1 T.

Results

The zero-field-cooled (ZFC)/field-cooled (FC) susceptibility data are shown in Fig. 2. In agreement with the previous investigations (Bernardini et al. 2000), the behaviour of the static susceptibility evidences a transition with antiferromagnetic nature: χ first increases with decreasing temperature, then reaches a maximum and finally decreases steadily. The value for the Néel temperature (T_N) has been refined to T_N = 6.1(2) K. A separation between the ZFC and FC curves is evident below T_N, when the two curves progressively split with decreasing temperature, thus suggesting a possible influence of the applied field (0.008 T) to the antiferromagnetic phase. However, the absolute value of the χ splitting is small: about 0.011 emu mol^{-1} at $T = 2$ K.

In order to characterise any possible dependence of the antiferromagnetic phase on the applied field, dynamic magnetisation measurements were performed above and below T_N. The *ac* susceptibility data are shown in Fig. 3, where both the real in-phase and the imaginary out-of-phase (Fig. 3) components (χ' and χ'', respectively) are reported, in arbitrary units, at different frequencies. While the behaviour of the static susceptibility appears quantitatively reproduced by the real component χ', no variations of the imaginary susceptibility are evident in the full temperature range, being χ'' constantly null. Moreover, no significant differences are found by varying the frequency of the applied field H(ω).

Figure 4 shows the high-field magnetisation (M) measurements performed on the powders up to 12 T at two different temperatures, 1.4 and 1.9 K, respectively. The behaviour of M versus H is almost linear within the investigated range, with only a small deviation at low magnetic field values (H $<$0.7 T). The small discrepancy, observable at the same H values, between the 1.4 and 1.9 K datasets, is within the experimental error. No evidence of high-field saturation of the magnetisation (Fries et al. 1997, Furdyna 1988) is visible.

Discussion

The comparison between the static and the dynamic susceptibility data suggests that the antiferromagnetic phase presents an ordered collinear structure. Even if the low-temperature discrepancy of the ZFC/FC data suggests a dependence of the static susceptibility on the applied field, the *ac* measurements definitely rule out the possible rise of frequency-dependent effects below the Néel temperature (Jonason et al. 1998). The

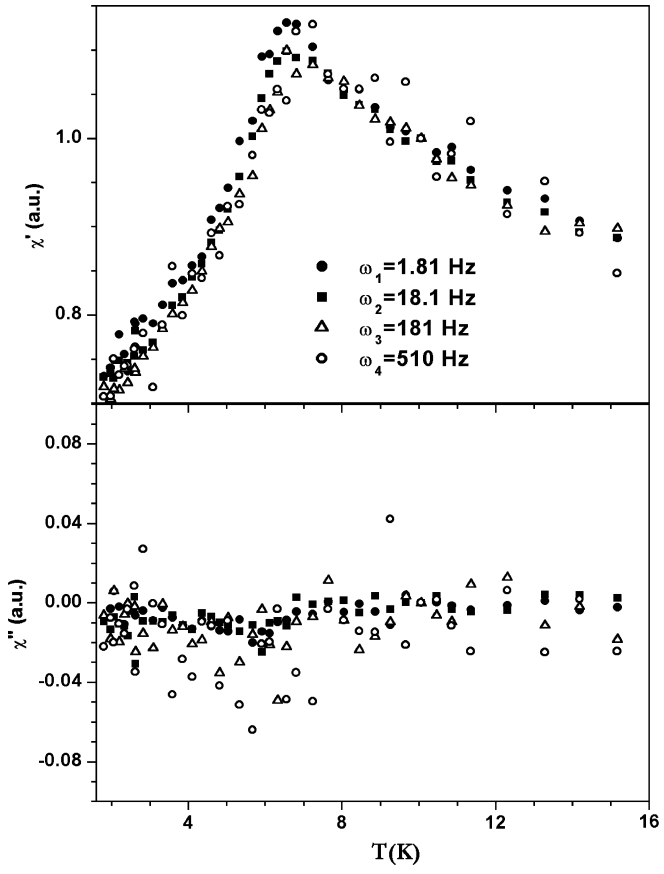

Fig. 3 *ac* susceptibility data: in-phase (χ') and out-of-phase (χ'') susceptibilities (a.u.) vs. T(K) at different frequencies

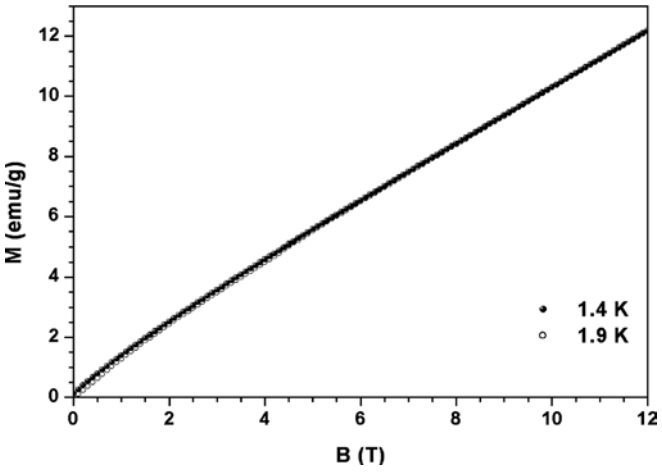

Fig. 4 M (emu g^{-1}) vs. B (T) data registered at 1.4 and 1.9 K

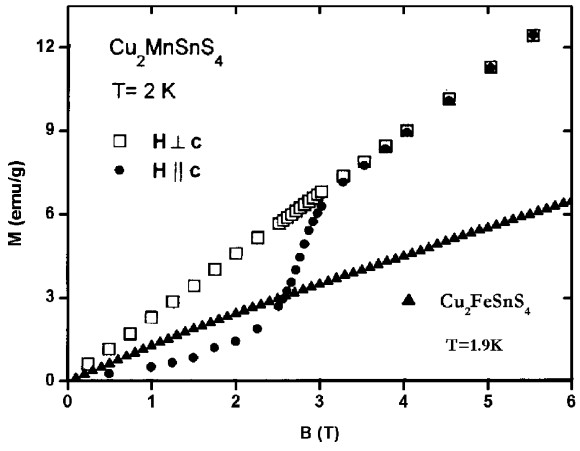

Fig. 5 M (emu g^{-1}) vs. B (T) data: comparison of the present result (*up triangles*) and of Fries et al.'s (1997) data on Cu_2MnSnS_4 (*open squares* and *circles*) at 1.9 and 2 K, respectively. (After from Fries et al. 1997)

out-of-phase χ'' component, in fact, is always negligible, and the coincidence of the static and dynamic χ' susceptibility is systematically observed. No dynamic properties, characteristic of a spin-glass phase, have been detected. The observed discrepancy of the static measurement may be explained taking into account a small drift of the temperature scale during the cooling process. As a consequence, Fe(II) ions in stannite belong, below T_N, to two antiparallel collinear sublattices, derived form their body-centred tetragonal crystallographic lattice, as occurs in other stannite-related compounds (Cu_2MnSnS_4, Cu_2MnGeS_4; Fries et al. 1997). The intersection of simple tetragonal sublattices, with the origins joined by a (1/2, 1/2, 1/2) vector, appears to be the most probable description of the antiferromagnetic structure (Fries et al. 1997).

The same authors evidenced, in Cu_2MnSnS_4 at 2.8 T, the presence of a "spin-flop" transition (Shapira and Foner 1969). Both the $H_{||}$ and $H_{\perp}$ behaviours (Fig. 6) were obtained, by means of single-crystal high-field magnetisation measurements. On the contrary, the present M v_s H data (Figs. 4, 5) do not evidence any, even small, transition up to 12 T. Nevertheless, the experimental slope is remarkably lower than the correspondent slope of Fries et al. (1997) for Mn, even if the observed susceptibility has been determined on powders (Carlin 1986). This relevant difference may be understood considering the spin-flop transition to occur at higher magnetic field values. According to this interpretation, the energy associated to the applied magnetic field, within the present experimental range, is not enough to break the antiferromagnetic alignment. This interpretation accounts also for the relevant difference between the Weiss constants, evaluated in the high-temperature regime (100–300 K) by Fries et al. (1997) and by Bernardini et al. (2000) for Cu_2MnSnS_4, −25(2) K, and Cu_2FeSnS_4, −64(1) K, respectively. The Weiss constant is, in fact, related to the exchange constant J in a mean-field approximation (Morrish 1966; Bernardini et al. 2000), and is therefore an indirect measurement of the strength of the antiferromagnetic interaction. The greater value, reported by Bernardini et al. (2000), confirms a stronger sublattice interaction, thus suggesting again the spin-flop transition to occur at high magnetic fields (> 12 T). However, the field of the

spin-flop transition, H_{SF}, depends on both the fields related to the exchange interaction, H_e, and to the magnetic anisotropy, H_a (Carlin 1986):

$$H_{SF} = \sqrt{H_e H_a - H_a^2} \ .$$

The exchange interaction does not increase enough to prevent the detection of the transition within the experimental magnetic field range: a ~3.5 higher H_e value (Fries et al. 1997; Bernardini et al. 2000) will determine a ~1.9 times increase in the H_{SF} value. An increase of the magnetic anisotropy is, therefore, to be considered. A large magnetic anisotropy is usual for high-spin tetrahedral Fe(II), due to the presence of a significant orbital contribution to the spin motion (Low and Weger 1960), which, on the other hand, is almost negligible for the high spin Mn(II), due to the high stability of its ground state (Fries et al. 1997; Furdyna 1988).

The present study of the low-temperature cusp of the susceptibility behaviour, observed for the synthetic analogue of stannite, evidences a transition from a paramagnetic to a long-range order antiferromagnetic phase. Two sublattices may be distinguished in the regular body-centred tetragonal disposition of Fe(II) ions, the interaction between which is remarkably strong, as confirmed by high-field magnetisation data, in agreement with Fries et al.'s (1997) and Bernardini et al.'s (2000) data.

Acknowledgements The authors wish to express their warmest thanks to G. P. Bernardini for the useful discussion and his critical reading of this manuscript. An anonymous referee, P. Léone and Y. Moëlo are sincerely acknowledged for their revision of the text. This work was partially financed by the MIUR ex 40%–2001 funds to C. Cipriani.

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