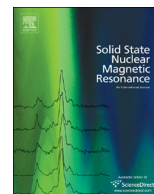




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## Solid State Nuclear Magnetic Resonance

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 $^{121,123}\text{Sb}$  and  $^{75}\text{As}$  NMR and NQR investigation of the tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) – Tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) system and other metal arsenides
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## ABSTRACT

This work is motivated by the recent developments in online minerals analysis in the mining and minerals processing industry via nuclear quadrupole resonance (NQR). Here we describe a nuclear magnetic resonance (NMR) and NQR study of the minerals tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ) and tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ). In the first part NQR lines associated with  $^{75}\text{As}$  in tennantite and  $^{121,123}\text{Sb}$  isotopes in tetrahedrite are reported. The spectroscopy has been restricted to an ambient temperature studies in accord with typical industrial conditions. The second part of this contribution reports nuclear quadrupole-perturbed NMR findings on further, only partially characterised, metal arsenides. The findings enhance the detection capabilities of NQR based analysers for online measurement applications and may aid to control arsenic and antimony concentrations in metal processing stages.

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## 1. Introduction

The mining industry's interest in tennantite (and similarly tetrahedrite) has been in the context of generally viewing these species as simultaneously both valuable and problematic. Although deposits of these minerals may contain economic copper grades, and remain attractive to process for this reason, they have a potentially large downside. When ores or mineral concentrates have significant arsenic they are normally subjected to additional treatment such as roasting stages, allowing arsenic capture (if the plant is on a sustainable footing). Otherwise the arsenic is released into the environment, which is becoming increasingly difficult to justify, even in developing world operations. Excess arsenic in mineral concentrates that are sent to smelters can lead to penalties for the mineral processor. Similar, although lesser, issues also apply to antimony.

There are several technological approaches that may be contemplated to reduce the concentrations of arsenic flowing into later-stage mineral and metal processing. For example, the online quantitative analysis of arsenic phases in crushed ore on primary conveyors may enable bulk ore sorting. In this approach, described in [1], ore pods with particularly high arsenic grade can be

diverted to dedicated special processing channels or retained as controlled stockpiles. A second approach involves the quantitative analysis of phases in mineral slurries to enable the advanced control of the mineral flotation process. With knowledge of the concentration of particular arsenic phases contained in the flotation process, flotation parameters may be adjusted to selectively float or suppress the key arsenic minerals [2], resulting in their subsequent removal from concentrates prior to smelting.

In either approach outlined above, a robust analytical measurement technique is required to determine the arsenic phase concentration in ore streams in an industrial setting. As discussed in [1] and references therein, zero-field magnetic resonance, such as NQR, is a promising technique for this purpose. However, the frequencies of the zero-field resonances in potential target minerals must obviously be known and resonance parameters characterised before they can be exploited for quantitative measurement. The laboratory work reported here is motivated by the requirement for selective online measurement of tennantite and tetrahedrite in ore streams.

Tennantite was first described for an occurrence in Cornwall, England, in 1819 and named after the Oxford chemistry professor, Smithson Tennant (1761–1815). Tetrahedrite is named more descriptively, getting its name from the distinctive tetrahedron shaped cubic crystals. The structure of tetrahedrite was first determined by Pauling and Neumann in 1934 [3] and subsequently refined [4]. Tennantite is a copper arsenic sulfosalt mineral with an

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ideal formula  $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ . A closely related mineral tetrahedrite ( $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) has antimony substituting for arsenic and the two form a solid solution series. The two minerals have very similar properties with a common structure and it is often difficult to distinguish between tennantite and tetrahedrite. Iron, zinc, and silver may substitute up to about 15% for the copper site.

In this work, we detail the existence of newly observed zero-field  $^{121,123}\text{Sb}$  and  $^{75}\text{As}$  resonances in these minerals at room temperature. In addition, we report NQR and nuclear quadrupole-perturbed NMR findings on  $^{61}\text{Ni}$ ,  $^{75}\text{As}$  and  $^{63}\text{Cu}$  in NiAs, NiAsS and CuAsS which complement the findings concerning tennantite and tetrahedrite.

## 2. Experimental

A combination of NMR and NQR was used to determine the NQR frequencies ( $\nu_{\pm m-1, \nu_{\pm m}}$ ) of the  $^{63,65}\text{Cu}$ ,  $^{75}\text{As}$  and  $^{121,123}\text{Sb}$  nuclei present in the specimens. Both  $^{63,65}\text{Cu}$  and  $^{75}\text{As}$  nuclei have nuclear spin  $I=3/2$  and only one NQR transition:  $m = \pm 1/2 \leftrightarrow m = \pm 3/2$ , where  $m$  is the magnetic quantum number, ranging from  $-I, -I+1, \dots, +I$ . The isotope  $^{121}\text{Sb}$  has  $I=5/2$  and two zero-field transitions  $m = \pm 1/2 \leftrightarrow m = \pm 3/2$  and  $m = \pm 3/2 \leftrightarrow m = \pm 5/2$  and  $^{121,123}\text{Sb}$  has  $I=7/2$  and three zero-field transitions  $m = \pm 1/2 \leftrightarrow m = \pm 3/2$ ,  $m = \pm 3/2 \leftrightarrow m = \pm 5/2$  and  $m = \pm 5/2 \leftrightarrow m = \pm 7/2$ . A complete exposition of the theory can be found in Slichter [5].

The high-field NMR spectra for  $^{63,65}\text{Cu}$  and the NQR spectra for  $^{121,123}\text{Sb}$  were obtained using a Bruker Avance 400 spectrometer with a 9.395 T magnet. The transmitter was broad banded and delivered high power pulses to a probe with a transversely oriented 9.5 turn 6 mm diameter Ag strip coil with a tuning range of 50–150 MHz. The  $^{63}\text{Cu}$  NMR spectra were acquired at a frequency stepped around a central 106.15 MHz and confirmatory  $^{65}\text{Cu}$  NMR spectra around a central 113.65 MHz. NQR spectra were obtained in the frequency range 50–110 MHz with the probe at 3 m distance from the magnet. Approximately 1.2 g powder specimens were loaded into black drinking straw containers (5 mm o.d.), plugged at each end with teflon tape. NQR investigations in the range 15–35 MHz used a home-made probe. High-field NMR powder patterns were analysed by the software package DMFIT [6] to determine the nuclear quadrupole coupling constant  $C_q$  and asymmetry parameter  $\eta$ .

Two specimens of tetrahedrite labelled tet1 and tet2, and one of tennantite labelled tenn1 were examined. The tet1 specimen was a natural mineral sample of unknown origin, ground to a particle size of 65  $\mu\text{m}$ . The specimen tet2 was from a tetrahedral shaped single crystal sourced from Mundo Nuevo, Sanchez Carrion Province, Peru, and ground to approximately 150  $\mu\text{m}$ . The tenn1 specimen was extracted from a larger hand specimen sourced from Tsumeb, Namibia, and ground to a particle size of 100  $\mu\text{m}$ . Prior to XRD analysis the samples were briefly further ground under ethanol in an agate pestle and mortar and then dried at 60 °C.

Powder XRD patterns were obtained using a Bruker D8 Advance X-ray diffractometer using  $\text{CuK}\alpha$  radiation. Analyses were performed on the collected XRD data using the Bruker XRD search match program Eva. The specimens were all highly crystalline. The tenn1 sample had minor constituents of sphalerite (cubic ZnS) and quartz ( $\text{SiO}_2$ ). The tet1 sample had a major impurity phase of quartz and a minor constituent of sphalerite. The tet2 sample had virtually no crystalline impurity constituents; its XRD pattern is displayed in Fig. 1.

The specimens were analysed by ICP-OES analysis to determine the Ag, As, Cu, Fe, Sb and Zn concentration. The results are expressed in units of weight% or parts per million (ppm) and are displayed in Table 1.

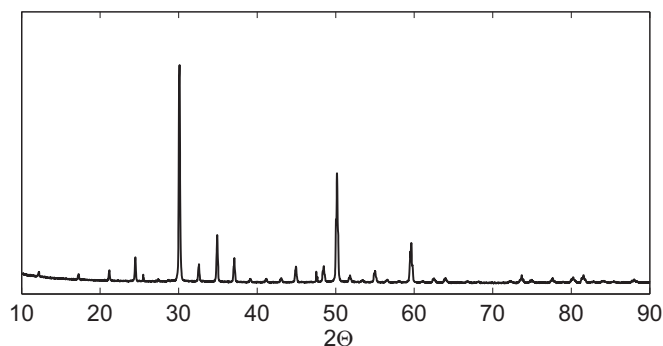


Fig. 1. Tetrahedrite (tet2): powder XRD pattern indicating a highly crystalline state; essentially single phase material.

Table 1  
ICP-OES analysis of selected samples.

Element	tet 1	tet 2	tenn1
Cu	24.4%	32.3%	36.5%
As	2.4%	8.5%	16.7%
Sb	15.2%	11.0%	0.22%
Fe	4.5%	1.3%	645 ppm
Ag	0.41%	0.12%	540 ppm
Zn	4.9%	7.5%	15.6%

## 3. Results and discussion

The Cu NMR spectra were investigated first. Tetrahedrite and tennantite are isostructural with space group  $I43m$  (#217) and a unit cell possessing two distinguishable Cu sites; one (Cu1) with tetrahedral S coordination  $\text{CuS}_4$  and the other (Cu2) with trigonal S coordination  $\text{CuS}_3$ . Cu1 has site symmetry  $\bar{4}$  (axial), while Cu2 has site symmetry 2 mm (non-axial); the Sb (As) has site symmetry  $\bar{3}m$  (axial). The site symmetry has implications for the electric field gradient (EFG) at the nuclear site. A site with axial crystallographic symmetry has an axially symmetric ( $\eta=0$ )  $\text{EFG} = e\partial^2V/\partial z^2$  [5], where  $V$  is the electrostatic potential at the nucleus. The quadrupolar splitting in nuclear resonance spectroscopy (NMR or NQR) is directly proportional to the EFG [5]. For example, for an  $I=3/2$  nucleus, such as  $^{75}\text{As}$  or  $^{63}\text{Cu}$ , the quadrupole resonance frequency  $\nu_q = (1/2h)e^2Q\partial^2V/\partial z^2 = C_q/2$ , where  $eQ$  is the quadrupole moment of the nucleus.

Gainov et al. [7] have reported the  $^{63}\text{Cu}$  nuclear quadrupole coupling for the  $\text{CuS}_3$  group in tennantite to be such that the frequency of resonance at 77 K is centred at  $^{63}\nu_q = 21$  MHz. The authors do not report observation of an NQR line from the Cu1 copper in irregular tetrahedral coordination by sulphur, but report speculation of a Cu1 NQR frequency below 4 MHz.

Since, for the two specimens of tetrahedrite examined here,  $^{65,63}\text{Cu}$  NQR scans in this region exhibited very low signal-to-noise ratio (s:n) at ambient laboratory temperature (295 K), a point by point  $^{63}\text{Cu}$  NMR scan centred at 106.15 MHz was undertaken for both tetrahedrite samples (see Fig. 2a). At this frequency, although the second order quadrupolar-perturbed lineshape (Q2) for the  $\text{CuS}_3$  site spanned only approximately 2 MHz, the s:n was much higher and it proved an efficient way of not only determining the value of the coupling constant, but also of estimating the value of  $\eta$ , which is not determined by NQR. A  $^{63}\text{Cu}$  point by point scan was also undertaken for tennantite (Fig. 2b). Analysis of the Q2 lineshape for tet1 and tet2 in Fig. 2a indicates for Cu2 a coupling constant  $^{63}C_q \approx 40$  MHz and  $\eta \approx 0.15$ . A similar analysis for tenn1 yielded  $C_q = 38$  MHz and  $\eta \approx 0$ . The values of  $C_q$  are consistent with the value at 77 K reported by Gainov et al. [7].

Near the centre of the Q2 NMR lineshape for Cu2 in both

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