

## Zero Field NMR and NQR measurements of natural copper minerals

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The copper magnetic resonance spectra in natural mineral specimens of chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ) and djurleite ( $\text{Cu}_{31}\text{S}_{16}$ ) have been measured. In chalcopyrite, shifting and asymmetric broadening was observed in several samples at room temperature and at 77 K which is attributed to Cu-Fe nonstoichiometry. Chalcocite and djurleite spectra at 77 K exhibit significant differences compared to previously reported spectra.

### 1. Introduction

Magnetic resonance in copper minerals falls into two broad classes. Minerals in the copper-iron-sulphur system which are comparatively rich in iron exhibit magnetic ordering at room temperature (RT). Examples include cubanite ( $\text{CuFe}_2\text{S}_3$ ) and chalcopyrite ( $\text{CuFeS}_2$ ). Local fields existing on Cu nuclei allow zero field  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  Nuclear Magnetic Resonance (NMR) measurements. The hyperfine field on copper nuclei in each mineral is determined by the particular Fermi contact terms, lattice dipole field etc, thereby producing transition frequencies that are highly specific. On the other hand, minerals in the copper-sulphur system, e.g., chalcocite ( $\text{Cu}_2\text{S}$ ) and djurleite ( $\text{Cu}_{31}\text{S}_{16}$ ), exhibit no magnetic ordering at room temperature and have relatively high  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  Nuclear Quadrupole Resonance (NQR) frequencies. These transitions result from electric field gradients at nuclei that arise from non-spherically symmetric copper coordination. The frequencies are strongly characteristic of a given mineral due to large electric field variations that result from subtle changes in bonding.

In this paper, a study of natural samples of chalcopyrite, chalcocite and djurleite is described. The study was undertaken to obtain a better understanding of the variability in measurement response across a range of natural samples, as well as to ascertain the physics underlying the response in natural samples.

### 2. Chalcopyrite ( $\text{CuFeS}_2$ )

Chalcopyrite ( $\text{CuFeS}_2$ ), with Néel temperature ( $T_n$ ) of 823 K, exhibits six resonances at room temperature [1], due to a local field of  $\sim 1.6$  T imposed on the copper nuclei. Each copper isotope ( $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ ,  $I = 3/2$ ) has a three line spectrum, consisting of a central transition, together with two quadrupole satellites. The magnetic resonance spectra are consistent with the known XRD result that each copper site in chalcopyrite is crystallographically equivalent and is coordinated in a slightly distorted tetrahedron.

The transition frequencies for multiple natural samples have been measured. The samples include powders obtained from mineral processing operations, together with specimens made up of large polycrystals. Most samples share the same transition frequencies and exhibit the  $^{63}\text{Cu}$  central transition at 18.46 MHz. However, for a few samples, the spectra show increased line broadening and shifting. Room temperature spectra corresponding to two samples, representing the extremes of the range observed thus far, are shown in Figure 1(a). Spectra were acquired point by point using composite averaged Hahn echo sequences at each measurement frequency. The blue trace shows the typical spectrum for most chalcopyrite samples studied. This particular sample was obtained from Mt Lyell, Tasmania. The red trace

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shows the spectrum of the second sample, obtained from Cobar, New South Wales, which is broadened and slightly upshifted in frequency. The broadening in the Cobar sample is asymmetric, with larger broadening on the higher frequency side of each resonance.

Figure 1(b) shows the spectra obtained at 77 K. All the transitions have higher frequency at 77 K, due to lower  $T/T_n$ . The average separation of the quadrupolar satellites ( $\Delta\omega_q$ ) in each sample, given in Table 1, show hardly any shift between the two temperatures. A striking feature of the spectra is the stronger broadening occurring at lower temperature for both Mt Lyell and Cobar samples. The Mt Lyell sample broadens by a factor of two, whereas the Cobar sample broadens by almost a factor of three compared to room temperature. The asymmetric broadening in the Cobar sample is more evident at 77 K. The shift between the two spectra increases by 0.3% between room temperature and 77 K.

Table 1. Comparison of decay times and line shifts in Mt Lyell and Cobar samples. Quoted  $T_1$ ,  $T_2$  and linewidths were measured on the  $^{63}\text{Cu}$  central transition.

	Mt Lyell (RT)	Cobar (RT)	Mt Lyell (77 K)	Cobar (77 K)
$T_1$ (ms)	18	15	50	43
$T_2$ (ms)	1.5	1.8	2	4.4
Linewidth (kHz)	120	250	240	800
$^{63}\text{Cu}$ $\Delta\omega_q$ (MHz)	4.4	4.3	4.6	4.5
Average line shift (%)	0.5		0.8	

Table 1 also shows comparison of transverse and longitudinal decay times, line shift and broadening for each case. The spin-lattice relaxation rate  $T_1$  was determined by plotting the copper nuclear spin echo magnitude as a function of the time delay between a saturating comb of 20  $\pi$ -pulses and a Hahn echo probe sequence. The spin-spin relaxation rate  $T_2$  was measured from a plot of the echo intensity as function of the delay time between the Hahn echo probing pulses. For all cases  $T_2^* \ll T_2$ , where  $T_2^*$  is the inverse linewidth parameter. Therefore most of the broadening is inhomogeneous. The lineshift and broadening observed in the Cobar powdered sample was also evident in unground samples, indicating that sample grinding effects were not significant. An electron-probe microanalysis of the samples show no significant differences in impurity levels of Mn, Al, Se or As, which exist at levels well under 100 ppm. XRD linewidths for each sample were very similar. Room temperature resistivity measurements of Cobar and Mt Lyell pressed powder indicated a decrease by a factor of two for the Cobar sample.

Chalcopyrite generally exhibits  $n$ -type semiconductor behaviour, with the highest conductivities obtained from iron-rich deposits. It has previously been suggested that the varying conductivity of natural chalcopyrite is due to variable nonstoichiometry, with Fe substituting for Cu, where Fe acts as an electron donor [2]. Previous studies of synthetically prepared chalcopyrite from metal rich mixtures also show higher levels of carrier concentration [3]. Relatively low levels of substitution (0.1%) are sufficient to explain the maximum number densities ( $\sim 10^{20} \text{ cm}^{-3}$ ) found in natural chalcopyrite samples.

Carrier concentration and substitution of paramagnetic impurities may explain some of the observations. Firstly, the polarisation of carriers in local fields that normally exist without impurities may contribute a hyperfine field (Knight shift) at Cu nuclei, e.g., by way of a contact term of  $s$ -orbital components of the carriers. Secondly, impurity centres may impart the carriers with an additional polarisation, which can also contribute to the hyperfine field. This can be important even at low impurity levels due to the long range polarising effects of the impurity. These results, particularly the asymmetric and temperature dependent broadening are reminiscent of observations in lightly doped metals and magnetically ordered materials, that is normally explained by the Ruderman-Kittel-Kasuya-Yosida (RKKY)

interaction [4, 5]. Both conventional Knight shift and the RKKY interaction can also lead to transition frequency shifts. It is supposed that the Cobar sample has increased carrier concentration or impurity substitution that could increase the relative shifting and broadening due to these two effects. This is supported by the increased conductivity observed for the Cobar sample. Also, the Cobar sample has co-crystallised cubanite (~10%), perhaps signifying a particularly iron rich environment.

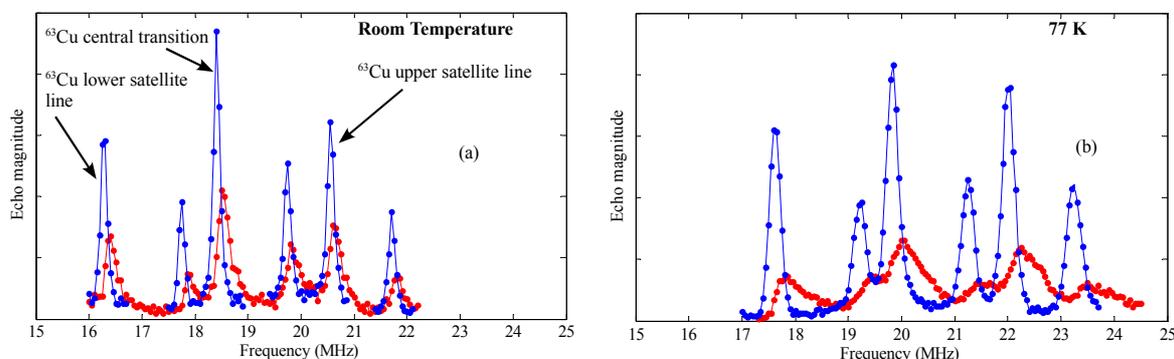


Fig 1. (a) The room temperature spectra of  $^{63,65}\text{Cu}$  in chalcopyrite. The blue trace corresponds to the Mt Lyell sample while the red trace corresponds to the Cobar sample. (b) Corresponding measurements of the two samples at 77 K.

### 3. Chalcocite ( $\text{Cu}_2\text{S}$ ) and Djurleite ( $\text{Cu}_{31}\text{S}_{16}$ )

Chalcocite and djurleite both exhibit complex structure that have some similarities. However they are distinct phases in the copper-sulphur system  $\text{Cu}_x\text{S}$ . At room temperature, chalcocite spans the stoichiometric range  $x = 1.997$  to  $2.000$ , while djurleite spans the range  $x = 1.934$  to  $1.965$  [6]. Detailed XRD studies [7] suggest that chalcocite and djurleite have 24 and 62 inequivalent copper sites, respectively. In chalcocite, the copper coordination is either trigonal or almost linear, with a range of Cu–S distances and various angles. In djurleite trigonal coordination dominates, but tetrahedral and linear coordination also occur. No structural phase transitions in either mineral below room temperature have been reported.

A thumbnail sized polycrystalline specimen of chalcocite was obtained from Bristol USA, a known chalcocite locality. A hand sized microcrystalline specimen of djurleite was obtained from Mt Gunson, South Australia. XRD analysis confirmed both the identification and high phase purity of each sample. Each specimen was hand ground before measurement. Figure 2(a) shows the chalcocite spectrum at 77 K, while Figure 2(b) shows the djurleite spectrum at both 77 K (blue trace) and 173 K (red trace). Numerous peaks spanning 15–26 MHz are visible in the spectra. Preliminary room temperature measurements were also performed on each sample. At least six narrow peaks remain observable in chalcocite at room temperature, whereas no lines were observed in djurleite. These room temperature results were also reproduced in other samples.

The frequency range of the response is within expectations for trigonally coordinated copper [1]. Based on the previous XRD structural analysis, there is an expectation of 48 lines in the chalcocite spectrum (24 sites, multiplied by two Cu isotopes) and 124 lines in the djurleite spectrum. However, some of the djurleite resonances corresponding to tetrahedrally coordinated copper should occur at lower frequency. Clearly, the broadening and complicated overlap in each of the spectra reported here prevents resolution of all lines. The spectral resolution at each measurement point is largely controlled by the pulse widths used in the echo sequence. For these data the pulse widths were 5 and 10  $\mu\text{s}$  respectively, corresponding to a spectral window of ~100 kHz for each point.

There are both similarities and significant differences between the results of this study and previous studies [1, 8]. The previous studies have attributed 48 lines to both chalcocite and djurleite spectra obtained at 77 K in the frequency range of 16–29 MHz. However many

peaks reported in the previous studies do not correlate with those reported here. While some of the discrepancy may be attributed to different broadenings in samples or experimental method, some peaks are difficult to reconcile.

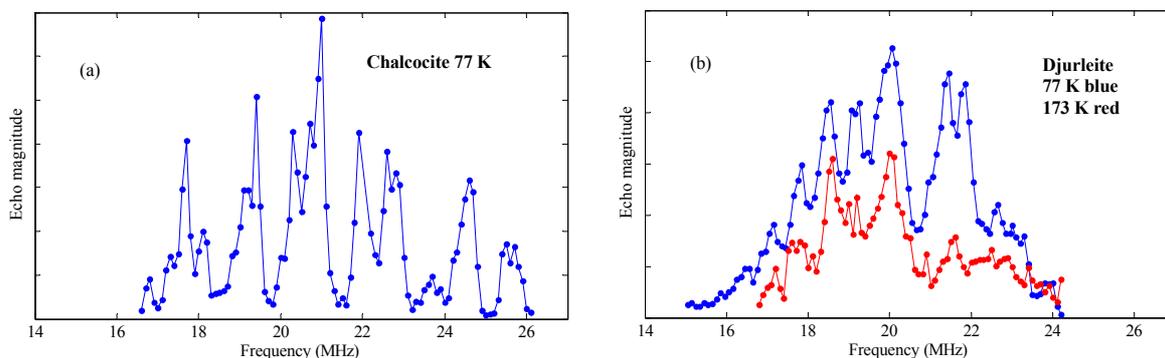


Fig 2. (a) The  $^{63,65}\text{Cu}$  NQR line spectrum of chalcocite measured at 77 K. (b) The  $^{63,65}\text{Cu}$  NQR line spectrum of djurleite measured at 77 K (blue) and at 173 K (red).

An interesting result observed in this study is that some chalcocite lines exist at room temperature. Previous work attributed the disappearance of chalcocite room temperature transitions to increasing ion conduction [1]. However, the djurleite spectrum disappeared entirely, despite lower ion conduction in this phase [9]. It would therefore seem difficult to ascribe ion conduction as the broadening mechanism in both cases. This explanation may be reconciled if line narrowing due to rapid ion motion occurs at higher temperature in chalcocite for particular sites. An alternative explanation is that hole carriers, known to be more numerous in djurleite [10] may also play a role in shortening transition lifetimes, as is the case for some NMR transitions in metals. To arrive at a better understanding of dynamics in these samples, additional work will be required to characterise decay times, resonances and conductivities across different lines and samples.

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