

THE MAGNETIC PROPERTIES OF METATORBERNITE

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ABSTRACT

The electron-spin-resonance spectra arising from the ^{63}Cu in metatorbernite exhibit strongly anisotropic g -factors and linewidths. The anisotropy is explained in terms of the magnetic interactions, which are strong *within* the planes containing the copper atoms and weaker *between* the planes.

Keywords: metatorbernite, g -factor anisotropy, electron-spin resonance, magnetic interactions.

SOMMAIRE

Les spectres de résonance de spin électronique provenant du ^{63}Cu de la métatorbernite se caractérisent par des facteurs- g et des largeurs de raie fortement anisotropes. L'anisotropie s'explique par les interactions magnétiques: fortes dans les plans qui contiennent les atomes de cuivre, faible entre ces plans.

(Traduit par la Rédaction)

Mots-clés: métatorbernite, facteur- g anisotrope, résonance de spin électronique, interactions magnétiques.

INTRODUCTION

Metatorbernite contains uranium, copper and phosphorus. The copper is divalent and hence paramagnetic. This property means that metatorbernite can be studied by electron-spin resonance (ESR). In this article we present the results of such a study and interpret these in terms of the crystal structure. The green color of this mineral arises mainly from the presence of divalent copper.

STRUCTURE AND X-RAY RESULTS

Metatorbernite belongs to the torbernite group of minerals, which is characterized by the formula $A^{n+}(\text{UO}_2\text{XO}_4)_2 \cdot n\text{H}_2\text{O}$, where A represents a cation and X is arsenic or phosphorus. This group contains phosphates and arsenates of uranium arranged in a laminar structure $(\text{UO}_2\text{XO}_4)_n^{n-}$. Metatorbernite,

with the chemical formula $\text{Cu}(\text{UO}_2\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and the structure sketched on Figure 1, crystallizes in the tetragonal system, space group $P4/nmm$ (D_{4h}^7), with two formula units per cell. Its crystal structure (Fron del *et al.* 1956, Ross & Evans 1964, 1965, Ross *et al.* 1964, Makarov & Tobelko 1960) has ^{63}Cu enclosed in a square planar configuration, with H_2O molecules providing very short Cu-O distances (1.91 Å). These short distances indicate the presence of very strong covalent bonds between the copper and oxygen atoms.

We selected for study large, well-formed crystals of metatorbernite on display at the McKissick Museum of The University of South Carolina. They were taken from the Wiseman mine in Spruce Pine, Mitchell Co., North Carolina in June 1932.

The structures of torbernite and metatorbernite are very similar, differing mainly in the number of water molecules. In the latter the number of water molecules varies between 8 and 12. In order to determine whether *our samples* are torbernite or metatorbernite, we carried out a X-ray-diffraction examination (powder pattern). The results were compared with the data of Fron del *et al.* (1956) and Ross *et al.* (1964).

ESR RESULTS

In this section we present the linewidth and gyromagnetic ratio obtained at room temperature with a Varian Model 4502 ESR spectrometer operating at a frequency of 9220 MHz using a power level of 250 mW with 100 kHz modulation.

A typical ESR spectrum for metatorbernite (Diaz 1981) is presented in Figure 2. The peak-to-peak linewidth depends on the orientation of the crystal, and varies between 0.02 and 0.034 Tesla. Such an effect is not unexpected for a layered structure of this type (Cheung & Soos 1978, Huang & Soos 1974). The calculated linewidth can be estimated from the expression of Anderson & Weiss (1953):

$$\Delta H = 2.3 (g \beta \rho) [S(S+1)]^{1/2} \times 10^{-4} \quad (1)$$

where $\beta = 9.27 \times 10^{-24}$ J/Tesla is the Bohr magne-

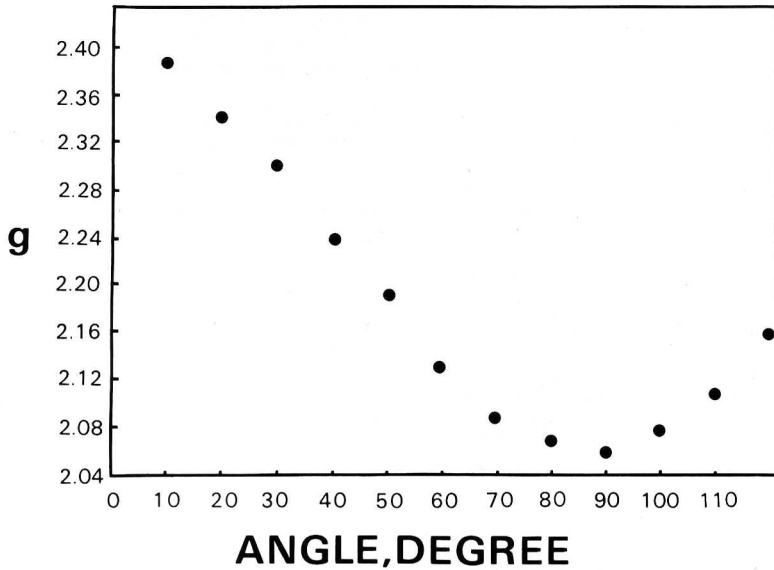


FIG. 3. Dependence of the g factor of ^{11}Cu in metatorbernite on the angle ψ relative to the c axis.

Following Cheung & Soos (1978) we can make use of the following expression for the linewidth of a two-dimensional system

$$\Delta H(\psi, T) = \frac{P(T)}{3 \cos^2 \psi - 1} - Q(T) \cos^2 \psi + R(T) \quad (4)$$

where ψ is the angle between the direction of the external magnetic field and the plane containing the ^{11}Cu atoms, and the temperature-dependent coefficients $P(T)$ and $Q(T)$ are determined experimentally. At ambient temperature we evaluated these coefficients from measurements made at three different angles, and this provided the following expression

$$\Delta H = [-5.94 (3 \cos^2 \psi - 1)^2 + 20.12 \cos^2 \psi + 25.64] \times 10^{-4} \quad (5)$$

This expression provided a good fit to the experimentally measured angular variation of the linewidth, shown on Figure 4; the experimental error in the measured linewidths is about 5%.

DISCUSSION

The structure of metatorbernite shows that the ^{11}Cu atoms are located fairly close together in planes that are separated by relatively large interpla-

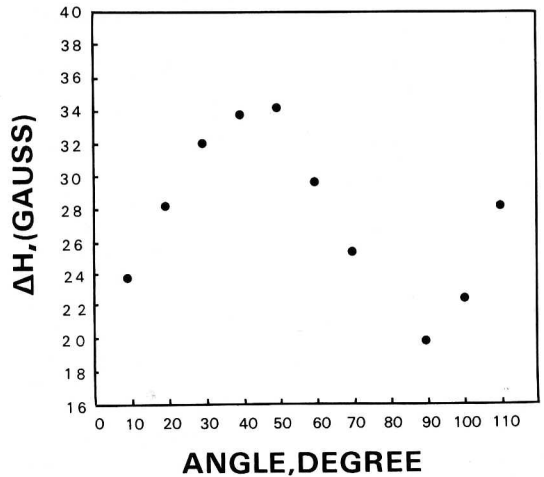


FIG. 4. Dependence of the linewidth ΔH or distance between the two peaks of the line ESR spectrum of ^{11}Cu in metatorbernite on the angle ψ relative to the c axis, where $1\text{G} = 10^{-4}\text{ T}$.

nar distances. This provides the possibility that the copper atoms form a two-dimension magnetic system that is exchanged-narrowed within the planes. Our experimental results demonstrate that this is the case. The narrowing of a line due to the exchange interaction has been observed and discussed by Huang & Soos (1974).

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