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THE MAGNETIC PROPERTIES OF METATORBERNITE

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ABSTRACT

The electron-spin-resonance spectra arising from the ^{II}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 résonnance de spin électronique provenant du ^{II}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, résonnance 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 $A^{n+}(UO_2XO_4)_2 \cdot nH_2O)$, where A represents a cation and X is arsenic or phosphorus. This group contains phosphates and arsenates of uranium arranged in a laminar structure $(UO_2XO_4)_n^{n-}$. Metatorbernite, with the chemical formula $Cu(UO_2PO_4)_2 \cdot 8H_2O$ 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 (Frondel *et al.* 1956, Ross & Evans 1964, 1965, Ross *et al.* 1964, Makarov & Tobelko 1960) has ^{II}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 Frondel *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):

$$\Delta H = 2.3\ (g\ \beta\rho)\ [\ S(S+1)\ ]^{½} \times 10^{-4} \qquad (1)$$

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

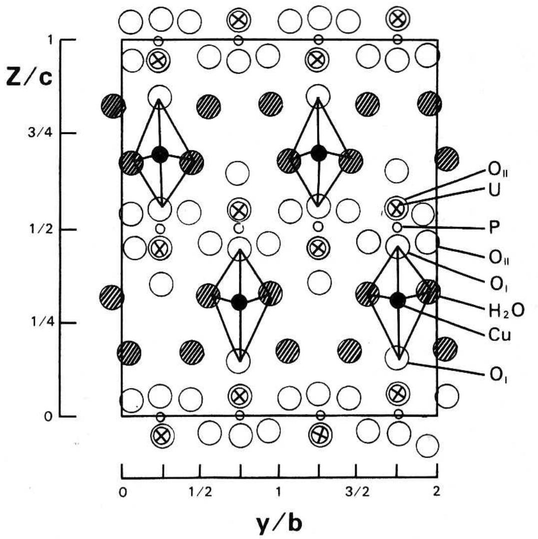

FIG. 1. Sketch of the locations of the various atoms in the crystal structure of metatorbernite. Projected in the *yz* plane, the copper atoms in the interplanar layers are shown located within distorted octahedra formed by square planar array of oxygen atoms from water molecules in the *xy* plane and oxygen above and below along the *z* direction. Two unit cells are shown.

ton, $g = 2.2$, $S = ½$ and ρ is the density of spins/m^3. Estimating ρ from the molecular weight (938) and the mass density 3.70 g/cm^3,

$$\Delta H = 96 \times 10^{-4} \text{ Tesla} \tag{2}$$

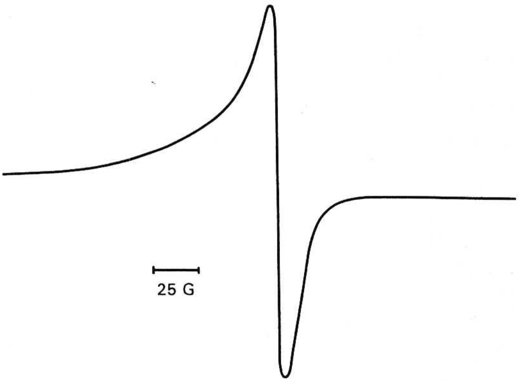

FIG. 2. Electron-spin-resonance spectrum produced by the ^{II}Cu atoms in metatorbernite, where 1G = 10^{-4} T.

which is significantly larger than the experimental values. This fact, together with the angular dependence of the linewidth and the layered structure of the mineral, suggests that we are dealing with a two-dimensional magnetic system, as will be explained in the next section.

The g factor is anisotropic and varies with the orientation of the crystal, between the values of 2.06 for g perpendicular to the *c* axis and 2.38 for g along the *c* axis, as shown on Figure 3. Values of g in this range are typical of those reported by various investigators for divalent copper (Diaz *et al.* 1971). A crystal-field-theory calculation (Poole & Farach 1972) made by us gave $g_{\parallel} = 2.16$ and $g_{\perp} = 2.03$, which differ considerably from the respective experimentally observed limiting values of 2.38 and 2.06. This discrepancy may be explained by the strongly covalent character of the copper–oxygen bonds.

LINEWIDTHS OF TWO-DIMENSIONAL MAGNETIC SYSTEMS

As mentioned above, each ^{II}Cu is centred inside a square of water molecules with very short Cu–O distances. These distances are so short that the copper–oxygen bonds are strongly covalent and the water molecules are highly polarized.

The uranium atoms lie along the *c* axis directly above and below the copper atoms, as indicated on Figure 1. As a result, there are nearby UO_2 groups that provide possible paths for superexchange interactions between the copper atoms. This causes the lines to be narrowed in accordance with the following expression

$$\Delta H = \Delta H_0 \left(\frac{g\beta\Delta H_0}{h/J} \right) \tag{3}$$

where J is the exchange-interaction frequency and ΔH_0 is the linewidth in the absence of exchange narrowing.

More importantly, we can also see from Figure 1 of Ross *et al.* (1964) that the copper atoms lie in planes with alternate interplanar separations of 6.58 and 10.73 Å. The four nearest-neighbor copper atoms all lie in the same plane. This causes the dipolar and exchange interaction to be dominated by the planar structure. Each copper ion is square planar co-ordinated with four oxygen atoms, thereby providing paths for the superexchange interactions, which narrow the lines. It therefore seems reasonable for the magnetic interactions to resemble those of a two-dimensional spin system.

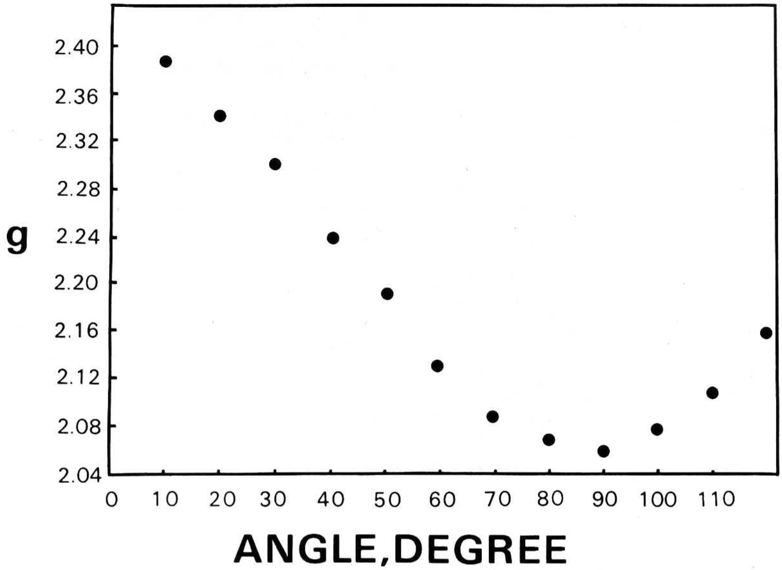

FIG. 3. Dependence of the g factor of ^{II}Cu in metatorbernite on the angle ψ relative to the c axis.

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

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

where ψ is the angle between the direction of the external magnetic field and the plane containing the ^{II}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

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

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%.

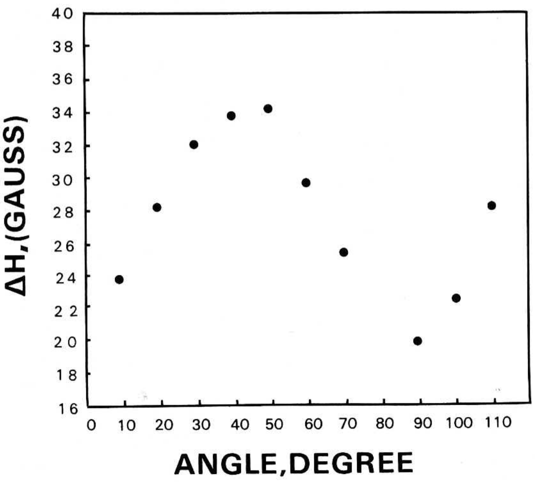

FIG. 4. Dependence of the linewidth ΔH or distance between the two peaks of the line ESR spectrum of ^{II}Cu in metatorbernite on the angle ψ relative to the c axis, where 1G = 10^{-4} T.

DISCUSSION

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