Clays and Clay Minerals, Vol. 24, pp. 211–212. Pergamon Press 1976. Printed in Great Britain

HYDRATION STRUCTURE OF EXCHANGEABLE Cu^{2+} IN VERMICULITE AND SMECTITE

(*Received* 9 *April* 1976)

The nature of adsorbed Cu^{2+} ions on various layer silicates has recently been investigated by electron spin resonance (esr) methods (Clementz *et al.*, 1973; McBride and Mortland, 1974; McBride *et al.*, 1975). An important result of these studies has been that the distorted octahedral $Cu(H_2O)_6^{2+}$ complex is oriented differently in smectite and vermiculite interlayers. This fact has been attributed at least partly to the strong interaction between the hydration water of Cu^{2+} and the vermiculite surface (McBride *et al.*, 1975). Thus, Cu^{2+}-saturated vermiculite has two interlamellar layers of water with the principal axes of the $Cu(H_2O)_6^{2+}$ ions oriented near 45° to the *ab* plane of the vermiculite planes (Clementz *et al.*, 1973). It is not known, however, if Cu^{2+} will orient similarly on vermiculites largely exchanged with other cations. In addition, there have been no comparisons made between the esr spectra of Cu^{2+} on vermiculites and smectites despite the different bonding environments expected for Cu^{2+} adsorbed on these two minerals. This study compares published esr data of exchangeable Cu^{2+} with data obtained on Cu^{2+}-doped vermiculite.

The high charge of Llano vermiculite in the tetrahedral layer (chemical formula given by Clementz *et al.*, 1973) requires that the average interionic distance between exchangeable divalent cations be ≈ 7 Å. Thus, broadening of the Cu^{2+} esr signal in Cu^{2+}-saturated vermiculite due to magnetic dipole–dipole interactions produces a poorly defined-spectrum (Clementz *et al.*, 1973). An attempt was made to produce a sharper spectrum by doping small amounts of Cu^{2+} into Na^+- and Mg^{2+}-vermiculite. Although the spectra obtained (Figs. 1, 2) were not as distinct as those recorded for Cu^{2+} doped into Mg^{2+}–hectorite (McBride *et al.*, 1975), they were detailed enough to permit calculation of the principal *g*-values and the hyperfine splitting parameters (*A*/*c*).

The Mg^{2+}–vermiculite, exchanged near the 5% level with Cu^{2+}, had a *d*(001) spacing of 14.2 Å as determined by X-ray diffraction on an oriented sample air-dried on a glass slide. The Cu^{2+} esr spectrum of this vermiculite (Fig. 1) demonstrated little orientation dependence as oriented vermiculite films were aligned in the magnetic field, *H*, by the method of Clementz *et al.* (1973). This result indicates that the $Cu(H_2O)_6^{2+}$ ligand axes are aligned near a 45° angle to the ab plane of the vermiculite. Evidently, $Cu(H_2O)_6^{2+}$ is oriented similarly in the vermiculite interlayer for both Cu^{2+}-saturated vermiculite and Cu^{2+}-doped Mg^{2+}–vermiculite. This result is expected, since the *d*(001) spacings of the Cu^{2+}– and Mg^{2+}–vermiculite are the same. There is some indication that the $g_\perp$ component of the esr spectrum is more intense when the *ab* plane of the vermiculite is parallel (∥) to the magnetic field, *H*, than when it is perpendicular (⊥) to *H* (Fig. 1). This suggests that the *z*-axis of $Cu(H_2O)_6^{2+}$ is inclined at an angle somewhat greater than 45° to the *ab* plane of vermiculite.

The Na^+–vermiculite, doped near the 5% exchange level with Cu^{2+}, had a *d*(001) spacing of 11.9 Å. The esr spectrum of an oriented film of this sample (Fig. 2) indicated, from the pronounced orientation dependence of the spectrum, that the *z*-axis of the hydrated Cu^{2+} was perpendicular to the vermiculite *ab* plane. This alignment is readily explained if it is concluded that hydrated Cu^{2+} ions must lose both axial water molecules, forming planar $Cu(H_2O)_4^{2+}$, in order to penetrate the interlayer of Na^+–vermiculite. The octahedral $Cu(H_2O)_6^{2+}$ complex, at the 5% level of exchange, is incapable of occupying an interlamellar region of Na^+–vermiculite composed of a monolayer of water molecules.

Solvents other than water can alter the interlamellar orientation of Cu^{2+} complexes on layer silicates (Berkheiser and Mortland, 1975). Thus, the Cu^{2+}-doped Mg^{2+}–vermiculite, when wetted in pyridine, produced a Cu^{2+} esr spectrum with the *z*-axis of the Cu^{2+}–pyridine complex perpendicular to the vermiculite *ab* plane. Since the *d*(001) spacing was 14.0 Å, it is likely that a planar Cu^{2+} complex with four pyridine molecules produced the orientation observed.

Comparisons between the Cu^{2+} spectra for vermiculite and smectite show some fundamental differences. The Cu^{2+}-doped Na^+–vermiculite and Cu^{2+}-doped Na^+–montmorillonite have similar *d*(001) spacings with planar $Cu(H_2O)_4^{2+}$ ions aligned in the plane of the approximate monolayer of interlamellar water (Table 1). Despite this stereochemical similarity of Cu^{2+}, the values of $g_\parallel$ and *A*/*c* are significantly different in the two minerals (Table 1). While $g_\parallel$ is larger in the vermiculite than in the montmorillonite, *A*/*c* is smaller in the vermiculite.

The Cu^{2+}-doped Mg^{2+}–vermiculite has a somewhat lower *d*(001) spacing than the Cu^{2+}-doped Mg^{2+}–hectorite, a fact that might be attributed to the different orientation of $Cu(H_2O)_6^{2+}$ in the two minerals. In hectorite, hydrated Cu^{2+} is oriented with the *z*-axis perpendicular to the *ab* plane (McBride *et al.*, 1975), while in vermiculite the *z*-axis is *near* 45° to the *ab* plane (Fig. 1). Also, $g_\parallel$ is larger while *A*/*c* is smaller for the Mg^{2+}–vermiculite compared to Mg^{2+}–hectorite (Table 1). It is apparent that

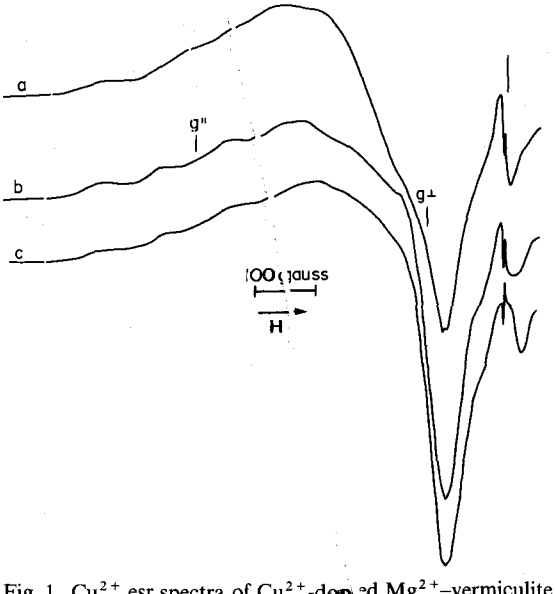


Fig. 1. Cu^{2+} esr spectra of Cu^{2+}-doped Mg^{2+}–vermiculite films (air-dry) oriented with the *ab* plane (a) 90° (⊥) (b) 45° and (c) 0°(∥) to the magnetic field, *H*. The positions of $g_\parallel$ and $g_\perp$ are indicated, and the free electron resonance position ($g = 2.00$) is indicated by a vertical line.

https://doi.org/10.1346/CCMN.1976.0240410 Published online by Cambridge University Press

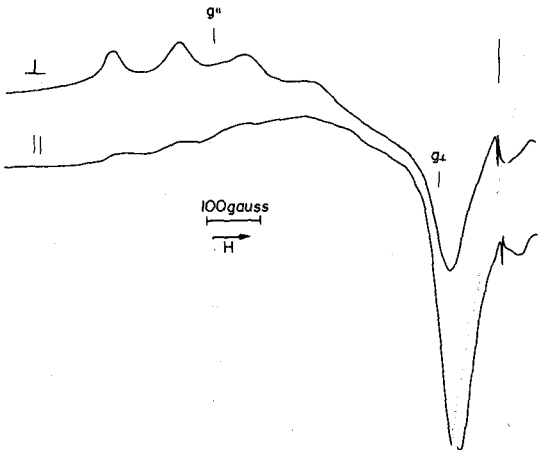


Fig. 2. Cu^{2+} esr spectra of Cu^{2+}-doped Na^{+}–vermiculite films (air-dry) oriented with the *ab* plane perpendicular ($\perp$) and parallel ($\parallel$) to *H*. Positions of $g_{\parallel}$, $g_{\perp}$ and $g = 2.00$ are indicated by vertical lines.

the properties of the layer silicate as well as the nature of the dominant exchange cation affect the bonding structure of Cu^{2+}.

The data of Table 1 reveal that, in general, $g_{\parallel}$ is larger and A/c is smaller for Cu^{2+} adsorbed on vermiculite compared to Cu^{2+} adsorbed on smectites. It has been shown that, as the Cu^{2+}–ligand bond becomes more covalent, $g_{\parallel}$ and $g_{\perp}$ must decrease while A/c increases (Kivelson and Neiman, 1961). The data suggest, then, that Cu^{2+} is more covalently bonded in Mg^{2+}–hectorite than in Mg^{2+}–vermiculite. A similar conclusion is implied for Cu^{2+} in Na^{+}–montmorillonite and Na^{+}–vermiculite (Table 1). The esr parameters for Cu^{2+} in aqueous solution ($-8°C$) have been determined to be $g_{\parallel} = 2.39$, $g_{\perp} = 2.07$, and $A/c = 0.0142\ cm^{-1}$ while in 60% glycerine–40% water ($-20°C$), the parameters have been calculated as $g_{\parallel} = 2.40$, $g_{\perp} = 2.10$, and $A/c = 0.0128\ cm^{-1}$ (Poupko and Luz, 1972). Since $g_{\parallel}$ is the most sensitive indicator of covalency (Kivelson and Neiman, 1961), it is concluded that aqueous Cu^{2+} resembles Cu^{2+} adsorbed on vermiculite more than Cu^{2+} adsorbed on smectites (see $g_{\parallel}$ values of Table 1).

Table 1. Esr and X-ray diffraction data for various air-dried layer silicates containing exchangeable Cu^{2+}

Layer silicate*	*d*(001) Spacing (Å)	$g_{\parallel}$	$g_{\perp}$	A/c (cm^{-1})
Cu^{2+}–hectorite†	12.4	2.34	2.08	0.0165
Mg^{2+}–hectorite‡ (~5% Cu^{2+}-doped)	15.0	2.335	2.065	0.0156
Na^{+}–montmorillonite (10% Cu^{2+}-doped)	(11.0)	2.33	2.08	0.0149
Cu^{2+}–vermiculite†	14.2	2.40	2.10	0.0115
Mg^{2+}–vermiculite (~5% Cu^{2+}-doped)	14.2	2.40	2.09	0.0123
Na^{+}–vermiculite (~5% Cu^{2+}-doped)	11.9	2.39	2.07	0.0138

* The montmorillonite used was the Upton, Wyoming clay and the vermiculite was from Llano, Texas. The unit cell formulae of these minerals are reported by Clementz *et al.* (1973).

† Data from Clementz *et al.*, 1973.

‡ Data from McBride *et al.*, 1975.

The bracketed *d*(001) spacing represents a randomly interstratified X-ray diffraction peak.

It is suggested that surface oxygen atoms of vermiculite, being capable of forming strong hydrogen bonds to water (Farmer and Russell, 1971), prevent maximum covalent bond formation between Cu^{2+} and the hydration water. The surface oxygens of smectite, having little capability to hydrogen bond, permit optimum covalent interaction between Cu^{2+} and water. As previous i.r. (Farmer and Russell, 1971) and esr (McBride *et al.*, 1975) spectroscopy have indicated, the position of charge in the layer silicates can thereby alter the orientation of hydrated cations on silicate surfaces. The strong hydrogen bonding of $Cu(H_2O)_6^{2+}$ and $Cu(H_2O)_4^{2+}$ in vermiculite may be the factor producing esr parameters similar to those for Cu^{2+} in aqueous solution. However, hydrated Cu^{2+} adsorbed on smectites can bond only weakly through its water molecules to the surface oxygens, and is chemically less similar to hydrated Cu^{2+} in solution.

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https://doi.org/10.1346/CCMN.1976.0240410 Published online by Cambridge University Press