shoulder and $^1A_{1g} \rightarrow {}^1A_{2g}$ for the higher energy band. The S-bonded isomer shows the splitting and low-energy shift since the ligand field strength of the ligand is substantially different from the other oxygen and nitrogen donor ligands.[14] Finally a prominent shoulder can be seen at 25.4 kK for the S-bonded isomer which is absent from the N-bonded isomer.

The ultraviolet spectra of the linkage isomers in methanol are quite similar with regard to the frequency of the charge-transfer band: $t_{2g} \rightarrow \pi^*$ at 29.8 kK and the acac$^-$ $\pi \rightarrow \pi^*$ band at 42.9 kK. A major difference, however, is the presence of an intense band at 39.4 kK (log (ϵ_{max} 3.75) in the spectrum of the S-bonded isomer. The band is absent or obscured by the acac$^-$ bands in the spectrum of the N-bonded form. An analogous band has been previously assigned[15] to a Co(III) → SCN$^-$ charge transfer for the S-bonded complex $[Co(CN)_5SCN]^{3-}$. The band at 39.4 and 25.4 kK for *trans*-[Co(acac)$_2$(SCN)py] may have a similar origin.

Comparison of the spectra of the N-bonded geometrical isomers shows the red shift of the charge-transfer and ligand band and the blue shift of the ligand field band normally seen in going from the cis to the trans isomers for bis(acetylacetonato)cobalt(III) complexes.[5]

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Registry No. *trans*-[Co(acac)$_2$(SCN)py], 51933-43-8; [Co$_2$(acac)$_4$(OH)$_2$], 51932-17-3; *trans*-[Co(acac)$_2$(NCS)py], 51933-44-9; *cis*-[Co(acac)$_2$(NCS)py], 52019-94-0.

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X-Ray Photoelectron Spectroscopy of Some Aluminosilicates

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Recently Urch and coworkers[1] have reported that the 2p ionization energy of aluminum having fourfold coordination in microcline, $KAlSi_3O_8$, is about 1.4 eV lower, as determined by X-ray photoelectron spectroscopy, than the 2p ionization energy of aluminum having sixfold coordination in Al_2O_3. Since the determination of the coordination of aluminum in soda–alumina–silicate glasses and in other noncrystalline materials is an important structural problem,[2] the ability to determine the coordination by photoelectron spectroscopy of core levels would be a significant accomplishment. The purpose of this study is to investigate the change in binding energy of the aluminum 2p core level as a function of coordination of the aluminum contained in aluminosilicate polymorphs. In particular, the 2p binding energies of aluminum contained in sillimanite and mullite, which are refractory minerals having about half the aluminum ions in fourfold coordination and the rest in sixfold coordination, have been determined and are compared to the binding energy of aluminum in kyanite in which the aluminum is only sixfold coordinated.

Table I. Corrected Core Electron Binding energies and Full Widths at Half-Maximum (FWHM) of Elements Contained in Aluminosilicates

Element	Electron level	Mineral	Binding energy (±0.5), eV	FWHM (±0.05), eV	Aluminum coordination
Al	2p	Kyanite	74.9	2.25	6-fold
O	1s	Kyanite	531.5	2.33	6-fold
Si	2p	Kyanite	103.0	1.95	6-fold
Al	2p	Sillimanite	74.9	2.16	50% 6-fold 50% 4-fold
O	1s	Sillimanite	531.5	2.62	50% 6-fold 50% 4-fold
Si	2p	Sillimanite	102.8	1.98	50% 6-fold 50% 4-fold
Al	2p	Mullite	75.0	2.28	41–56% 6-fold 59–44% 4-fold
Al	2s	Mullite	119.6	2.66	41–56% 6-fold 59–44% 4-fold
O	1s	Mullite	531.8	2.79	41–56% 6-fold 59–44% 4-fold
Si	2p	Mullite	103.2	2.41	41–56% 6-fold 59–44% 4-fold

Experimental Procedure

The elemental electron binding energies were measured with a McPherson ESCA 36 photoelectron spectrometer using unmonochromatized Al Kα X-radiation for photoelectron excitation. Compensation for sample charging was made by measuring the binding energies relative to a C 1s energy of 285.0 eV. The carbon is due to residual vacuum pump vapor collecting on the sample surface in the vacuum chamber of the spectrometer.

Kyanite and sillinmanite, both Al_2SiO_5, were selected from relatively massive, high-purity minerals. The mullite sample is a commercial material whose X-ray pattern indicated a major mullite phase and a minor glass phase. All of the aluminum in kyanite is in sixfold coordination,[3] whereas the aluminum ions in sillimanite are equally divided among sites having fourfold and sixfold coordination.[4] The aluminum in mullite is also distributed between fourfold and sixfold coordinations,[5] with 41–56% of the aluminum having sixfold coordination. The exact percentage of aluminum in sixfold coordination in mullite depends on the ratio of alumina to silica.

In order to obtain relatively uncontaminated surfaces that are truly representative of the bulk aluminosilicates and from which reproducible spectra can be obtained, the brittle crystalline aluminosilicates were fractured under vacuum by a device that has been specifically designed to fracture brittle materials in the vacuum chamber of the McPherson photoelectron spectrometer.[6] Prior to being mounted in the fracture device, the crystalline materials were cut to the proper shape and were slotted so that the location of the fractured surface could be controlled.

The observed spectral lines were deconvoluted using a computer deconvolution program based on a Simplex pattern search and by assuming a single gaussian distribution. A good fit to the experimental data was observed in all cases.

Results and Discussion

The uncorrected aluminum 2p spectra obtained from the three aluminosilicates are shown in Figure 1, and the corrected electron binding energies along with the full widths at half-maximum obtained by a computer fit of the data

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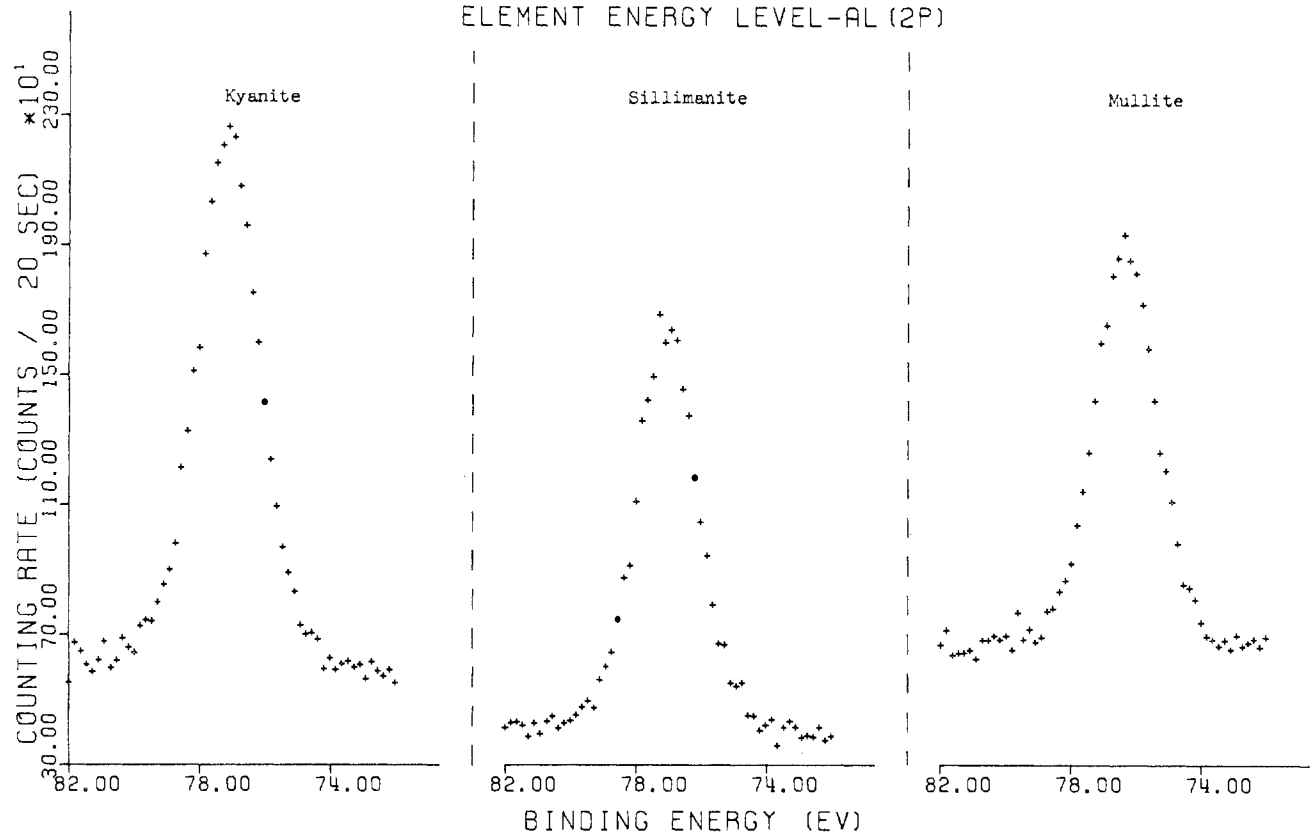

Figure 1. Photoelectron spectra of kyanite, sillimanite, and mullite.

are listed in Table I. As can be seen from Figure 1 and Table I, the binding energies and full widths at half-maximum of the aluminum 2p level are quite similar for the three materials. Indeed, the full width at half-maximum (FWHM) of the 2p level of aluminum in sillimanite, which possesses both fourfold and sixfold coordinations, is actually somewhat less than the FWHM of the 2p level of aluminum in kyanite, which has all of its aluminum in sixfold coordination. The core electron binding energies of oxygen and silicon are also observed to be the same within experimental error. The FWHM of the oxygen 1s and the silicon 2p levels of mullite are observed to be larger than the same levels in the other two aluminosilicates, but this may be due to the existence of the minor glassy phase, which is presumably SiO_2, in addition to the mullite phase.

Although the 1.4-eV difference in the 2p binding energy of aluminum in microcline has been attributed to the different coordinations of the aluminum in the two compounds,[1] it can also be explained by using ionic model concepts. Sixfold coordinated aluminum has been shown to have a 2p binding energy that can vary by as much as 1.6 eV depending on the number of positively charged ions in the lattice.[7] The presence of additional potassium cations in the crystal lattice of microcline, $KAlSi_3O_8$, has the effect of reducing the electron-attracting ability of the oxygen atoms. This causes a decrease in Al 2p binding energy as the number of positively charged ions increases and could account for the Al 2p binding energy in microcline being 1.4 eV lower than it is in alumina. However, when materials have similar chemical compositions, this effect will be absent and binding energy shifts due only to differing coordinations can be unambiguously determined. Sillimanite and kyanite, both Al_2SiO_5, meet this requirement. Since the Al 2p spectrum for sillimanite, with the aluminum in both fourfold and sixfold coordinations, is essentially identical with that for kyanite, with aluminum only sixfold coordinated, it must be concluded that photoelectron spectroscopy of core levels is unable to differentiate between aluminum atoms in different coordinations. This conclusion is strengthened by the data for mullite which is also essentially identical with that for kyanite even though the aluminum is again both fourfold and sixfold coordinated.

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Registry No. Kyanite, 1302-76-7; sillimanite, 12141-45-6; mullite, 1302-93-8.

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Discovery of Monoamminepalladium(II) Chloride Using Thermogravimetry

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Several workers have studied the thermal decompositions and isomerizations of a number of palladium-ammine complexes.[1,2] The most extensive studies of the thermal decompositions of tetraamminepalladium(II) chloride and