

smaller interaction. For alloys with small M content such as A_5M the interaction seems to be too small for a formation of ordered alloys with cubic close packing because of the entropy at elevated temperatures, where A and M are mobile.

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Polarized X-ray Absorption and Double Refraction in Vanadyl Bisacetylacetonate

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Abstract

X-ray dichroism is observed in crystalline vanadyl bisacetylacetonate, $\text{VO}^{2+} \cdot 2(\text{C}_5\text{H}_7\text{O}_2)^-$, near the vanadium K edge in absorption experiments with linearly polarized synchrotron radiation. The Kossel

structure is polarized as a result of the symmetries of molecular orbitals in this strongly anisotropic molecule. The extended X-ray absorption fine structure is polarized because of the difference in distance to the axial and equatorial oxygen neighbors. In this wavelength region, the anomalous-scattering terms and

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the index of refraction vary with the direction of polarization. Some of the consequences and possible applications of these properties are discussed.

Introduction

In this paper, we report some observations of the variation of X-ray absorption in crystals of vanadyl bisacetylacetonate according to the direction of the electric vector of the photon. This polarized absorption or dichroism is the result of two distinct phenomena which involve the symmetry of unoccupied molecular orbitals and the geometry of neighbor atoms. It may be used to study the geometry, orientation and electronic structure of molecules. It gives rise to X-ray double refraction and anisotropy of anomalous scattering which introduce interesting complications into the X-ray optical and diffraction properties of the crystal.

The existence of polarization effects in the X-ray absorption fine structure is predicted by theory (Azároff & Pease, 1974; Stern, 1974) both for the Kossel structure near the edge and for the extended structure (EXAFS). There have been several reports (reviewed by Azároff & Pease) of the observation of small differences of amplitude or wavelength for the fine structure of simple metals or salts. More recently, Heald & Stern (1977) observed polarized absorption effects for the Se *K*-edge white line and for the EXAFS structure at both the Se *K* edge and the W *L*₃ edge in the layered compound WSe₂. This phenomenon has been exploited to study the orientation of bromine adsorbed on graphite (Heald & Stern, 1978).

We became interested in the absorption fine structure while studying anomalous X-ray scattering, which is another manifestation of the same electronic phenomena which are involved in the absorption process. The anomalous-scattering terms f' and f'' are related to the absorption cross section σ by the relations (James, 1962; Wagenfeld, 1975)

$$f''(\omega) = mc\omega\sigma(\omega)/4\pi e^2, \quad (1)$$

$$f'(\omega) = (2/\pi) \int_0^{\infty} [\omega' f''(\omega')/(\omega^2 - \omega'^2)] d\omega', \quad (2)$$

where the Cauchy principal value is taken for the integral in (2). By virtue of these relations, the white lines which occur at some absorption edges (so named because they are so strong that they appear white when recorded photographically) are accompanied by exceptionally large changes in anomalous scattering. We demonstrated that these large changes occur and that their effects can be measured in the diffraction intensities in the case of the cesium *L*₃ edge in cesium hydrogen tartrate, where f' reaches $-26e$ and f'' $+16e$ (Phillips, Templeton, Templeton & Hodgson, 1978). Any other fine-structure feature will be associated with

similar variations of the anomalous scattering, but often the magnitudes of the effects will be much smaller.

In seeking examples of novel and extreme anomalous-scattering behavior which we might study by the same techniques, we learned of the sharp absorption line which occurs in advance of the main *K* edge in various vanadium compounds including vanadyl salts and complexes (Zhurakovskii & Vainshtein, 1960; Best, 1966; Hodgson, 1978). We recognized that the highly anisotropic structure of the vanadyl ion might give rise to significant polarization effects, and that any such effect would complicate the measurement of anomalous scattering even with unpolarized radiation. The highly polarized nature of synchrotron radiation (electric vector in the plane of the electron orbit) would accentuate such effects and also facilitate their detection. The triclinic structure of vanadyl bisacetylacetonate, in which all the molecules are parallel or antiparallel, is advantageous for investigating anisotropic molecular properties (Dodge, Templeton & Zalkin, 1961), and it has already been used to study magnetic anisotropy (Gregson & Mitra, 1973) and polarized infrared absorption (Adams & Trumble, 1975).

Experimental

The experiments made use of a Nonius CAD-4 diffractometer with radiation focused by a doubly curved mirror and made monochromatic by reflection from two germanium crystals (Hastings, Kincaid & Eisenberger, 1978; Phillips, Templeton, Templeton & Hodgson, 1978) at the Stanford Synchrotron Radiation Laboratory. This apparatus, designed for recording single-crystal diffraction intensities, is mounted with its θ and ω axes horizontal to permit measurements of 90° scattering of the horizontally polarized synchrotron radiation. To permit calibration of the monochromator wavelength setting, which lacks an absolute zero-angle datum, the computer control system includes provision for scanning an absorption curve. A helium-filled ion chamber before the diffractometer measures the initial intensity, and the diffractometer scintillation counter, set at zero angle, records the transmitted intensity. Ordinarily, a polycrystalline sample is inserted between the two detectors, and the position of an absorption edge is used to set the wavelength scale.

In these experiments a crystal of vanadyl bisacetylacetonate, VO(C₅H₇O₂)₂, with dimensions 1.0 × 1.2 × 1.5 mm, was mounted on the diffractometer as the absorber. Its orientation with respect to the diffractometer coordinate system was determined using a large collimator and high-angle Bragg reflections. Absorption curves (Figs. 1 and 2) were recorded using a 0.4 mm collimator, which gave a small enough beam

to be eclipsed by the crystal. The diffractometer software, which accepts fractional values of hkl , permits the setting of the V—O bond vector into a vertical position for the 'perpendicular' experiment. The vector components must of course be expressed in the reciprocal-lattice coordinate system. The rotation into the horizontal ('parallel') position is calculated using the Eulerian geometry system of the diffractometer. This rotation is about the beam direction as an axis, so that in principle the X-ray paths are identical. Some imperfection in the mechanism or alignment resulted in a somewhat longer effective mean path length for the perpendicular case as judged by the attenuation remote from the absorption edge. The curves have been normalized to diminish this effect, but the normalization is likely to be imperfect. The energy scales of the various curves are equal with high precision but lack a high-accuracy absolute calibration. The pre-edge line in the 'parallel' curve is a marker which may be used to tie the energy scale to other work.

Polarized Kossel structure

As shown in Fig. 1, the absorption line at 5466 eV nearly disappears when the electric vector is perpendicular to the molecular axis. Because the X-ray beam is not perfectly polarized and because some of the molecules in the absorber may not be perfectly oriented, we cannot be sure that there is any perpendicular absorption for this line, excluding the residual absorption from the outer electrons. Several spectra measured for other orientations of the crystal verify that the absorption depends on the direction of the electric vector and not on the path direction, with inter-

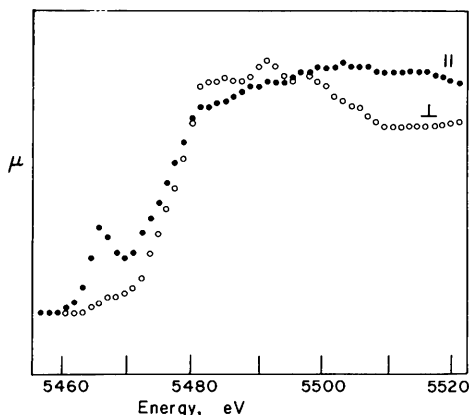


Fig. 1. Absorption coefficient (on an arbitrary scale) versus photon energy for vanadyl bisacetylacetonate; linearly polarized X-rays with electric vector parallel (black circles) and perpendicular (open circles) to the short V—O bonds.

mediate intensities at intermediate angles of polarization. The width of this line (about 5 eV at half height) is due to the finite wavelength spread of the radiation which results from the effect of the focusing mirror; it has been observed as about 2 eV wide at half height with the more nearly monochromatic radiation of another beam line and a polycrystalline sample (Tullius, Carlson, Gillum & Hodgson, 1978).

This polarized line must result from excitation of a 1s electron into a vacant molecular orbital. In an isolated atom the allowed transitions are to vacant p states, but such an atomic description would not explain the polarization nor the sensitivity of this line to the chemical state of the vanadium. Ballhausen & Gray (1962) have described the electronic structure of the vanadyl ion coordinated to five water molecules in a distorted octahedral structure with C_{4v} symmetry. This model, with neglect of the fifth water molecule, is a good approximation of the coordination in the present compound. In C_{4v} symmetry, the allowed transitions are to a_1 states with parallel polarization and to e states with perpendicular polarization. Ballhausen & Gray find an antibonding orbital, designated $1a_1^*$, made up of a combination of vanadium $3d(z^2)$ and $4s$ wave functions with a σ orbital of the vanadyl oxygen atom, which is calculated to lie at -8.5 eV. This orbital seems to be the most plausible final state for our polarized line. The transition to the $3d$ or $4s$ states in the absence of mixing with the oxygen orbital is not allowed, but mixing with the oxygen orbital gives the hybrid the necessary p character. This model explains the absence of this absorption in trivalent vanadium compounds (Hodgson, 1978) which lack the close oxygen neighbor.

Inspection of Fig. 1 suggests another unresolved absorption at 5475 eV which is also parallel polarized. There is an excess of perpendicular absorption around 5485 eV, followed by an excess of parallel polarization around 5510 eV. We postpone a discussion of these features because higher resolution experiments are in order, and we hope to undertake them.

This dichroism will not occur in highly symmetrical molecules such as permanganate ion, which has a similar resolved pre-edge line (Hanson & Beeman, 1949), but it may be commonplace in less symmetrical molecules. A search for other examples seems worthwhile. Several applications can be suggested. The polarization properties will help test theoretical models for the molecular electronic structure. The angular variation of the intensity of the absorption line is a probe which can be used to measure the molecular orientation of vanadyl ions, or distribution of orientations, in an anisotropic specimen, whether crystalline or not. This crystal may be used as a polarizing filter to modify or detect the state of polarization of an X-ray beam (but only at these limited wavelengths). Other consequences to X-ray optics and to anomalous scattering are discussed below.

Polarized extended X-ray absorption fine structure

Scattering of the photoelectrons from neighboring atoms, the oxygen atoms in this case, gives rise to the diffraction ripples in the EXAFS region (Fig. 2). The theory of this effect is described by Stern (1974). The contributions of the neighbors are additive and depend on the radial distance, the thermal motion, a back-scattering amplitude characteristic of the neighbor atom, and phase shifts which are characteristic of the atomic identities of both the absorbing atom and the neighbor atom. Teo & Lee (1979) have calculated and tabulated the amplitude and phase functions for numerous elements. The polarization effect arises out of a factor $\cos^2 \theta$, where θ is the angle between the electric vector of the X-ray and the direction of the neighbor atom.

The crystal structure of vanadyl bisacetylacetonate (Dodge, Templeton & Zalkin, 1961) has been redetermined using diffractometer technique (Ruben, Templeton & Templeton, unpublished; $R = 0.059$ for 2200 reflections). Each vanadium atom has five oxygen neighbors at the corners of a nearly square pyramid. The vanadyl oxygen atom, at a distance 1.581 (2) Å, lies at the apex of this pyramid, and this axial V—O bond is the reference vector for our discussion of the polarization effects. The four oxygen atoms of the acetylacetonate ligands, at the corners of the pyramid base, are at distances ranging from 1.963 (2) to 1.971 (2) Å. Their V—O bonds make angles 104.8, 105.0, 107.0 and 107.4° with the axial bond.

In the approximation of an ideal square pyramid, if α is the bond angle of the four basal oxygen atoms to the axis and β is the angle of the electric vector to the axis, then the sum of the four $\cos^2 \theta$ terms is

$$4 \cos^2 \alpha \cos^2 \beta + 2 \sin^2 \alpha \sin^2 \beta \quad (3)$$

by a simple calculation in spherical trigonometry. The rotational symmetry has removed any effect of the azimuthal angle of the polarization vector; in other words, the optical effect is uniaxial. If $\alpha = 106^\circ$, as in our example, this function is maximum when $\beta = 90^\circ$ (the perpendicular setting) and minimum at $\beta = 0^\circ$. The ratio of these extremes is 6.08. On the other hand, the axial oxygen atom contributes according to $\cos^2 \beta$, which is zero for the perpendicular setting and maximum for the parallel setting. Other factors in the theory enhance the effect of atoms at shorter distances, so that the axial neighbor is expected to dominate the parallel absorption fine structure.

Using the phase-shift functions of Teo & Lee (1979) for V and O, we calculated the energies at which maxima and minima occur in the EXAFS spectra due to V—O distances of 1.58 and 1.97 Å; these energies are marked by arrows in Fig. 2 on the parallel and perpendicular curves, respectively. As explained by Teo & Lee, there is ambiguity in the proper choice of E_0 , the

threshold energy for the photoelectric effect, according to what phase-shift functions are used. To achieve the fit observed in Fig. 2, we used $E_0 = 5490$ eV. One may notice that the positions for some of the peaks and valleys are quite different for the two polarizations, and that in line with the above analysis the longer bond length fits the perpendicular curve, while the shorter one dominates the other.

This relatively crude experiment was not designed to be a definitive study of the EXAFS effect, but it gives a hint of the power that single-crystal polarized EXAFS spectroscopy may have for studying phase-shift phenomena, for resolving small differences in neighbor distances, or for learning the coordination geometry of atoms in complex structures which have not yielded to X-ray diffraction analysis. A similar technique may be useful in the study of oriented but non-crystalline materials, such as biological fibers or membranes.

In reference to anomalous scattering and X-ray diffraction, one can say that measurable EXAFS effects will occur in almost any crystal at some wavelength, and that polarization effects will occur whenever the local symmetry is not too high. Generally, the magnitudes will be small enough to be neglected in crystal structure analysis as currently practiced. However, one should look for effects in special cases such as uranium or yttrium compounds studied with Mo $K\alpha$ radiation or compounds of gadolinium, dysprosium or cobalt studied with Cu $K\alpha$ radiation. A disagreement with the theoretical value of

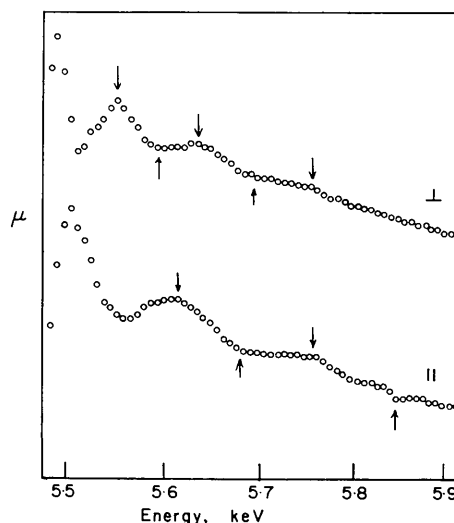


Fig. 2. Polarized EXAFS spectra for vanadyl bisacetylacetonate; electric vector perpendicular (top curve) and parallel (bottom curve) to the short V—O bond. The arbitrary absorbance scale is magnified about double that of Fig. 1 and is displaced for the two curves. The slope of the smooth background absorption is partly the result of instrumental effects. Arrows mark values for the positions of maxima and minima calculated as described in the text for V—O distances of 1.97 (top curve) and 1.58 Å (bottom curve).

f'' for cobalt at Cu $K\alpha$ has already been reported (Templeton, Zalkin, Ruben & Templeton, 1979).

X-ray double refraction and anisotropic anomalous scattering

According to (1) and (2), any polarization of the absorption cross section will cause f'' at the same wavelength and f' at neighboring wavelengths to have values which change according to the orientation of the electric vector. The index of refraction n is related to the scattering factor $f = f_0 + f' + if''$ (James, 1962);

$$n = 1 - (2\pi Ne^2/m\omega^2)f. \quad (4)$$

Thus, the index of refraction depends on the direction of the electric vector: in other words, the crystal is birefringent for X-rays.

In principle, the X-ray optical properties of vanadyl bisacetylacetonate are biaxial, as in the visible region, but it seems likely that the uniaxial model used in the above discussion is adequate for practical purposes. For example, if the carbon atoms give significant EXAFS effects a biaxial description is required, but these effects are expected to be small. In either case, an X-ray beam penetrating the crystal will be split into a parallel ray and a perpendicular ray, one being more strongly attenuated than the other. To calculate a diffraction intensity one must use different values of f' , f'' , the absorption correction, and the polarization factor for each ray. The polarization factor becomes more complicated than in the usual case and depends on the state of polarization of the incident beam, the orientation of the optic axis (or axes), and the direction of the diffracted ray. An interesting consequence is that a horizontally polarized X-ray beam can scatter at 90° in the horizontal plane for some orientations of the crystal. This effect is exactly analogous to the depolarizing effect of a doubly refracting crystal between crossed polarizers. These effects introduce formidable complications into diffraction experiments and the experimental determination of anomalous scattering.

Further complications, not yet completely analyzed, occur when the crystal contains several molecular orientations, as in most of the known vanadyl salts. Then, each molecular orientation must be assigned its two values of each anomalous-scattering term. An interesting result, which begs for experimental verification, is that the screw-axis and glide-plane rules for absent reflections are no longer rigorous since crystallographically equivalent atoms do not have exactly the same scattering power. An estimate of the magnitudes

indicates that the intensities of such violations of the space-group extinction rules will be weak.

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