

be flat and less than 0.5 mm thick throughout most of its length. The conus is 2.5 mm long and 4.0 mm wide across the anterior edge, and has a depth of 2.0 mm. No other features of the shell are evident. The radiographs (Fig. 4) show spots within the shell area, but spots of similar shape and density are also seen outside of the shell and are probably small bodies of pyrite. The shell appears to be complete but fractured.

The nature of the shell and its small size relative to the arm crown leave little doubt that the shell was internal, and that the animal was a coleoid. The presence of a small open conus and the lack of a phragmocone suggest that the shell may be a teuthid gladius. However, it appears not to be differentiated into median field and wings, as in the teuthids, nor are two of the arms modified as grasping tentacles, as in most teuthids and sepiids. Arms of essentially equal length, with hooks in double rows, are belemnite and phragmotooth characters, although the shell is unlike that of either of these groups.

If a teuthid or a sepiid, *Jeletzkyia* is certainly the oldest representative of the modern squids, previously known

from the Early Jurassic onward. The discovery of such a creature in the Paleozoic was anticipated by Jeletzky. In a recent monograph he stated his belief that "now-known taxa of fossil belemnite-like and teuthid Coleoidea, other than the Jurassic and Cretaceous belemnites proper, represent only a very small percentage of the taxa that actually lived in Middle to Late Paleozoic, Mesozoic and Cenozoic seas" (5).

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4. We are grateful to Dr. Rainer Zangerl and Mrs. Ida Thompson for making the radiographs.
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Solid-State Energy-Dispersion Spectrometer for Electron-Microprobe X-ray Analysis

Abstract. Improved lithium-drifted silicon solid-state detectors allow detection and energy dispersion of x-rays of about 3 to 30 kiloelectron volts in the electron-microprobe x-ray analyzer. Energy resolution is sufficient to separate peaks of characteristic x-rays of elements adjacent in the periodic system at atomic number 20 and higher. The detected x-ray spectrum emitted from an unknown sample can be recorded with a multichannel analyzer in approximately 60 seconds.

In electron-microprobe x-ray analysis, a focused electron beam is used to excite characteristic x-ray spectra in sample volumes of a few cubic microns; the intensity of the characteristic x-rays is a function of element concentration. For qualitative and quantitative elemental analysis, characteristic x-rays are selected with crystal x-ray spectrometers. These spectrometers separate the x-ray emission, according to wavelength, by diffraction from a crystal (wavelength dispersion) and commonly cover a wavelength range from about 1 to 88 Å (12 to 0.15 keV).

Detection and separation of x-ray spectra can also be achieved by use of energy-dispersion characteristics of certain types of x-ray detectors, where the

amplitude of the detector output signal is proportional to x-ray photon energy. The main advantage of energy dispersion over wavelength dispersion is its ability to detect all lines in the emission spectrum simultaneously and with high photon-counting efficiency. Gas proportional detectors were first used for energy dispersion in electron-microprobe analysis by Dolby (1) and Birks and Batt (2). The method is limited by the resolution of the gas proportional detector—approximately 1.3 to 1.8 keV for $\text{CuK}\alpha$ radiation. Resolution is defined as the width of the measured x-ray line at half the height of the peak above background.

Solid-state detectors with significantly higher resolution (1.1 keV) have recently been applied to x-ray photon

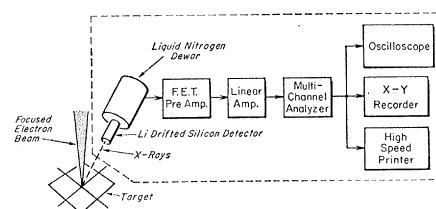


Fig. 1. Solid-state energy-dispersion spectrometer.

counting (3). We now describe the application of such a detector (manufactured by ORTEC), having a resolution of 0.6 keV, to an ARL electron microprobe (4). This higher resolution substantially improves separation of characteristic x-ray lines in complex x-ray spectra, and line-to-background ratios.

The solid-state energy-dispersion spectrometer (Fig. 1) consists of a cooled lithium-drifted silicon diode, a low-noise preamplifier (ORTEC 116), a linear amplifier (ORTEC 440), a multichannel (1024) analyzer (Nuclear Data 2200), and a high-speed printer (Franklin 1220). The detector and first stage of the preamplifier, cooled by liquid nitrogen, are mounted inside a separate vacuum chamber which is isolated from the main vacuum of the electron probe by a 0.125-mm beryllium window.

The detector is mounted in an existing x-ray port of the electron-microprobe analyzer, 25 cm from the target, at an x-ray emergence angle of 52.5 deg. The active area of the detector is 0.5 cm², with an active depletion depth of 2 mm. The preamplifier is a charge-sensitive field-effect transistor having low noise-high gain characteristics; it is closely coupled to the detector and provides gain to the detector signal and impedance matching to the linear amplifier. Gain and pulse shaping of the preamplified signal is accomplished by the linear amplifier. The amplified output signal from the linear amplifier is coupled to the analog-to-digital converter of a multichannel analyzer that processes pulses according to height (that is, energy) and stores them in the appropriate memory location. The stored energy spectrum can then be displayed on an oscilloscope screen for visual inspection, printed out on a high-speed printer, or plotted as an analog signal on an x-y recorder.

Performance of the solid-state energy-dispersion spectrometer (resolution and line-to-background ratio, sensitivity, and energy range) was evaluated with pure-element targets.

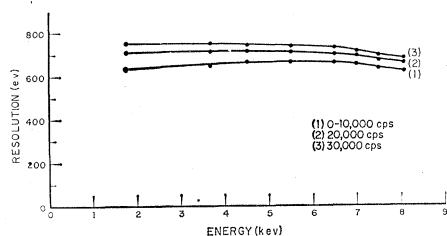


Fig. 2. Resolution of energy-dispersion spectrometer as a function of x-ray photon energy and count rate.

Resolution was measured by recording characteristic x-ray lines of these elements; expressed as full width of the peak at half-maximum, it is plotted (Fig. 2) as a function of wavelength and counting rate. The resolution of the spectrometer was nearly constant for a wide range of energy, with a slight dependence on counting rate above 10,000 counts per second (5).

The spectrometer was not equipped with precision d-c restoration, which, if employed, would allow count rates of 25,000 counts per second without loss of resolution (6). The x-ray photon count rate for each element was regulated to specific values by adjustment of the target current. Electronic shaping times of 2 μ sec were used in the linear amplifier to obtain maximum resolution. Resolution is limited at the lower counting rates mainly by the noise in the first stage of the pre-amplifier, and at higher counting rates

by pulse pileup in the electronics.

Figure 3 illustrates the energy range, separation, and peak-to-background ratios with the present resolution, obtained for x-ray lines of elements adjacent in the periodic system; the upper spectra were obtained with an accelerating potential of 35 keV and target currents of 1 and 5 na for the $L\alpha$ and $K\alpha$ x-ray lines, respectively. An accelerating potential of 20 keV and a target current of 1 na were used in obtaining the lower spectra. Peak-to-background ratio is given in parentheses for each peak.

Although the peak-to-background ratios are considerably lower than those commonly obtained with crystal spectrometers, they are significantly better than those obtained by energy dispersion with gas proportional detectors, which in similar applications typically have line-to-background ratios of 8:1 for copper $K\alpha$ radiation.

The usefulness of this particular spectrometer for low-energy x-rays is limited by the noise amplitude and by the transmission of the 0.125-mm beryllium window to approximately 3.7 keV ($CaK\alpha$). X-rays of still lower energy are detected (for example, $SiK\alpha$, 1.7 keV), but resolution for these energies is insufficient for separation of, for example, $SiK\alpha$ from $PK\alpha$. The high-energy limit of x-ray photons that can be detected with the solid-state energy-dispersion spectrometer is determined by the accelerating potential

of the electron beam (commonly between 30 and 50 keV) rather than by any limitations of the detector.

The results of our study show that lithium-drifted silicon solid-state detectors are superior in performance to gas detectors in the energy range from 3.0 to 30 keV. The improved resolution of an energy-dispersion spectrometer equipped with a solid-state detector adds versatility and analytic capability to the electron-microprobe x-ray analyzer. The particular advantage of such a spectrometer is that qualitative analysis of samples of unknown composition is obtained in tens of seconds. Complete spectra emitted from a sample may be recorded and then displayed on an oscilloscope screen for rapid visual inspection, or recorded in digital form for further evaluation by computer. Many of the readout techniques developed for electron-microprobe analysis in recent years [for example, electron-beam scanning and concentration mapping (7)] can be performed with this type of spectrometer in less time than with a crystal spectrometer. Energy-dispersion spectrometers detect x-rays without regard to direction of the incoming photon; thus large off-axis deflection of the electron beam (for example, beam-scanning analysis) can be tolerated without loss of intensity.

As a consequence of the high collection efficiency of solid-state energy-dispersion spectrometers (about 80 percent), electron-microprobe analysis may be accomplished with sufficient counting statistics at lower incident electron beam currents than is possible with a crystal spectrometer. Lower currents may enable analysis of samples that are altered by electron beams of higher current densities.

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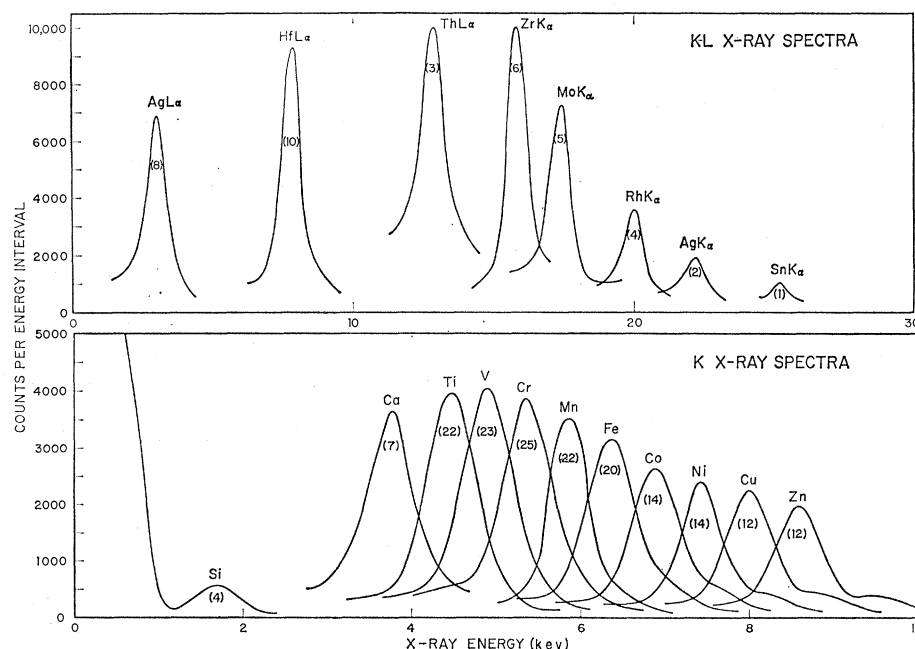


Fig. 3. Composite of pure-element spectra obtained by solid-state energy-dispersion spectrometer in electron-microprobe x-ray analyzer. Peak-to-background ratios are given in parentheses; integration time, 100 seconds.

typical of characteristics of resolution by the detector, but is attributed to partial resolution of the $K\beta$ line and to electronic effects.

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Superconductivity and Antiferromagnetism in Boron-Rich Lattices

Abstract. *Ferromagnetism, antiferromagnetism, or superconductivity has been discovered in most hexa- and dodecaborides.*

Superconductivity, ferromagnetism, or antiferromagnetism has been found in most metallic hexa- and dodecaborides. The temperatures of superconduction and magnetic transition are given in Table 1. This is the first time that superconductivity has been discovered in boron-rich compounds.

Boron itself is nonmetallic in all elemental modifications, yet the specific resistivities of hexa- and dodecaborides at low temperatures are below those of

most transition-metal compounds. There is even a slight resemblance between the the antiferromagnetic and the superconducting transitions. At or below the Néel point, the electric resistivity drops abruptly, a feature which recently, in the case of NdB_6 , may have been mistaken for superconductivity itself (1). Antiferromagnetism and a not quite so drastic drop in resistivity have been found previously for GdB_6 by Coles (2). We have found similar behavior for all magnetic rare-earth compounds investigated except the EuB_6 (Table 1), whereas all corresponding nonmagnetic rare-earth compounds become superconducting. The nonmagnetic tetraborides, which are equally good metallic conductors, showed no superconducting transition above 0.35°K .

Specific heat data have been obtained for both YB_6 and ZrB_{12} . The expected anomalies associated with the transition into the superconducting state were observed for both compounds. The very sharp transition observed for ZrB_{12} is shown in Fig. 1. The extrapolated electronic heat capacity coefficient per mole of ZrB_{12} (13.55×10^{-4} calories mole $^{-1}$ deg $^{-2}$) is almost exactly twice that found for one mole of YB_6 . Consequently, both compounds have the same value of slightly over 1×10^{-4} calories deg $^{-2}$ per gram atom of boron.

The compounds described are, from an atomistic point of view, mostly boron. It was therefore tempting to consider the above results as indicative of the behavior of a hypothetical cubic boron lattice which is metallic. The aforementioned properties exist only when we have three-dimensional cubic arrays, which are characteristic of the hexa- and dodecaborides.

The tetraborides being tetragonal are structurally intermediate between the two-dimensional MB_2 and the three-dimensional MB_6 arrangement (3). They no longer show any superconducting transitions above 0.35°K . The absence of superconducting transitions in one- and two-dimensional lattices has been pointed out earlier for covalent borides (4) and the graphite intercalation compounds (5). The existence of superconductivity found only in the hexa- and dodecaborides again confirms the validity of the empirical result that superconductivity exists only in three-dimensional structures.

A certain formal analogy exists between these borides and the beryllides. The formulas of the latter range from MBe_{12} to MBe_{22} , M being almost any

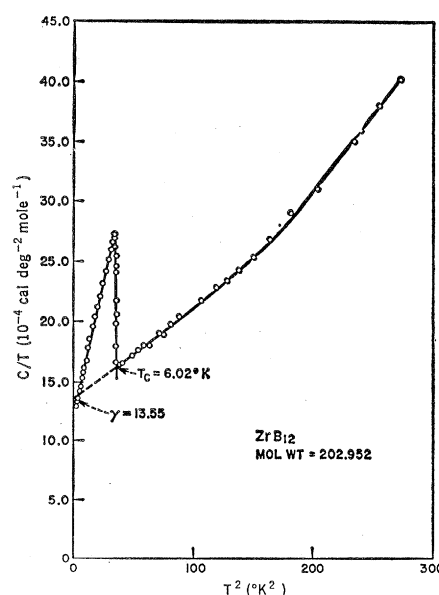


Fig. 1. Specific heat as a function of temperature for ZrB_{12} .

transition element. Most of the MBe_{22} compounds, if not all, also exhibit superconductivity (6), which might be considered typical for the body-centered cubic phase of beryllium (7). The electronic specific heat of these Be compounds is very low and in the order of 0.1×10^{-4} calories per gram atom of Be, whereas for the hexa- and dodecaborides it is an order of magnitude higher. Thus we conclude that cubic metallic boron, should it ever come into existence, would have an appreciable electronic specific heat.

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Table 1. Superconducting, antiferromagnetic, and ferromagnetic transitions of hexa- and dodecaborides. X-ray diffraction data for hexaborides sometimes showed small amounts of tetra- and dodecaborides. For T_{sc} (superconductivity), sharp transitions $\approx 0.1^\circ\text{K}$ wide were observed at 16 kc/sec unless otherwise indicated. Néel transitions identified by the abrupt decrease in resistivity as discussed in the text are given in column R; those identified by an abrupt decrease in susceptibility (measured by an inductive method at 25 cycle sec $^{-1}$) are given in column χ .

Compound	T_{sc} ($^\circ\text{K}$)	$T_{N\acute{e}el}$ ($^\circ\text{K}$)		T_{Curie} ($^\circ\text{K}$)
		R	χ	
ScB_{12}	0.39			
YB_6	6.5-7.1			
YB_{12} *	4.7			
ZrB_{12}	5.82			
LaB_6 *	5.7			
CeB_6		3.0	3.0	
PrB_6		7		
NdB_6		8.6	8.6	
EuB_6				8
GdB_6		17.6	17.5	
TbB_6		23	23	
DyB_6		21.5	21	
HoB_6		9		
HoB_{12}			6.5	
ErB_{12}			6.5	
TmB_{12}		4.2		
LuB_{12}	0.48			
ThB_6	0.74			

* Incomplete superconductive transitions indicate that not all the sample was superconducting.