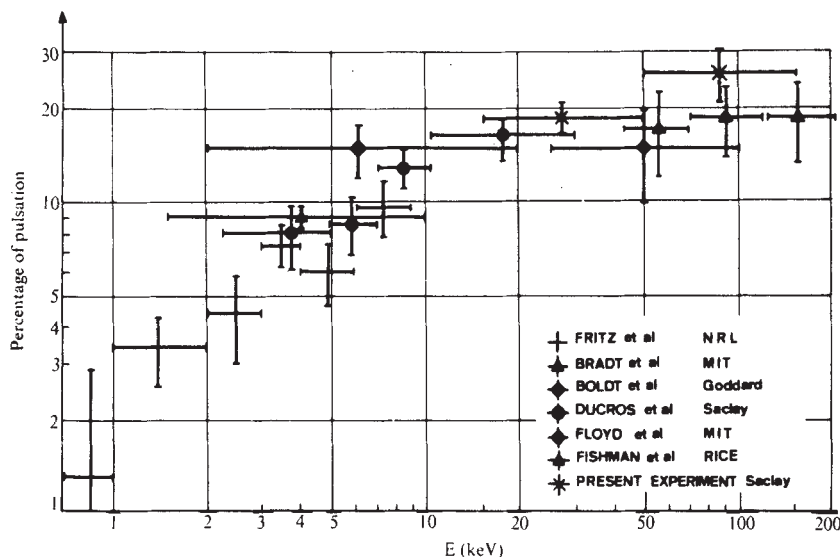Fig. 5 Variation in pulsation rate as a function of energy.

12.5 ± 0.5 ms, a value consistent with optical and soft X-ray observations. Table 3 gives the arrival time of the main pulse for each flight.

The phase was computed using the best fitting phase formula $N = E + At + Bt^2 + Ct^3$ for pulsar ephemeris[8]; t is the time elapsed between the epoch of the adopted ephemeris and the arrival time of the main pulse, computed in a reference frame bound to the barycentre of the solar system. The absolute error in the computed phase is due to the definition of the profile (66 channels of approximatively 0.5 ms). The X-ray phase is clearly in good agreement with the optical phase.

Between flight 1 (September 15, 1970) and flight 2 (September 22, 1970) a "jump" in the velocity of the Crab Nebula wisps (on September 20, 1970) was reported by Scargle at the 1970 Austin meeting. No significant change after the "jump" can be observed, taking into account timing uncertainties.

During one flight a French–Italian γ-ray group was observing the pulsar NP 0532 in the energy range > 50 MeV. Correlated data and phase comparison are to be published.

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Positional Disorder in the A-Site of Clino-amphiboles

THE crystal structures of several sub-calcic amphiboles have been refined and some details of the A-site chemistry are presented in this communication. The A-site is located in the octahedral layer of the amphiboles and is sandwiched between two infinite Si_4O_{11} silicate chains from the adjoining tetrahedral layers. The site has symmetry $2/m$ and is in general coordinated by 12 oxygens. The site may be empty, partially occupied or fully occupied in order to satisfy any charge imbalance resulting from cationic substitution on the M (octahedral) and T (tetrahedral) sites. When occupied it contains only monovalent Na^+ and K^+ cations. Highly anisotropic electron density has been observed on the A-site in the refinements of kakanui hornblende and potassium richterite[1] and has been interpreted as positional disorder about the special position within the mirror plane.

During the refinements of ferrotschermakite, barkevikite and ferrohastingsite the isotropic temperature factors of the A-site cation were 5.4, 6.4 and 6.1 A^2 respectively. These were considered as unreasonably large when compared with temperature factors of Na^+ and K^+ in other well-refined silicates[2–4]. Serial section Fourier maps showed two sets of symmetrically unrelated maxima about the special position, one set confined to the mirror plane and the other set along the two-fold axis. Corresponding difference Fourier maps showed high residual density displaced from the special position, both in the mirror plane and along the two-fold axis. These features could be masked by artificially raising the temperature factors; in this case the electron density highs became smeared and in the extreme cases resulted in a high residual on the special position. Obviously the elimination of systematic errors in the data is extremely important in order to resolve these features.

The coordinates of the A-site maxima were taken from the Fourier maps and these were used as the input parameters to a structure factor calculation for a positionally disordered model. An immediate reduction in the R-factor was apparent, which was marginally significant for ferrotschermakite but highly significant for barkevikite and ferrohastingsite at the 0.005 level using Hamilton's tests[5]; these differences in significance reflect the higher partial occupancy of the A-site in barkevikite and ferrohastingsite. One cycle of least squares varying the positional parameters produced a reduction in the R-factor that was highly significant for all three structures. A further reduction in the R-factor was accomplished by including the temperature factors and the occupancies as variables in the refinement; the occupancies were constrained to the total site chemistry[6] as determined from the chemical analysis.

The A-site cations show a strong fractionation into the set of disordered positions within the mirror plane as with the kakanui hornblende and potassium richterite; in the kakanui

hornblende a significant amount of electron density was also observed along the two-fold axis[1]; however, the positions and occupancies were not refined. It has been suggested that the occupancies of the two sets of disordered positions correspond to the amounts of Na^+ and K^+ in the structural formula; this correlation was not observed in the three new refinements where it seems that the size of the cation is not the chief feature in determining its position in the A-site. It has also been suggested[7] that the direction of disordering (that is in the mirror plane or along the two-fold axis) is controlled by the O(3) anion which may be OH^- or F^-; this effect, however, is precluded in the case of the three amphiboles at present under investigation due to the insignificant amounts of F^- in them.

As suggested by Papike et al.[1], it is considered that one of the principal factors controlling this positional disorder must be the A1 occupancy of the T sites and the concomitant charge balance requirements of the coordinating oxygens. This interpretation is, however, hampered by a lack of information on the distribution of tetrahedral A1 over the T(1) and T(2) sites. Another factor that must be considered is the cation–cation repulsion effect between the A-site cations and the multivalent octahedral cations. This effect will to some extent depend on the site-fractionation of the octahedral cations. Further work is in progress which hopefully will provide enough data to unravel the cause of positional disorder in the clino-amphibole A-site.

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Surface and Interfacial Energies in Systems of Certain Refractory-metal Monocarbides with Liquid Cobalt

ONE technique for the determination of surface energies of solids is the method of multiphase equilibrium[1,2]. This method has been used in the past to measure the surface energy of the compounds UO_2 (ref. 3) and UC (ref. 4), as well as that of metals[2]. Briefly, the method involves the measurement of certain equilibrium interphase angles, namely (i) the angle of contact, θ, of a suitable liquid on the surface of the solid in a suitable atmosphere; (ii) the dihedral angle, φ, formed in a system of grains of the solid dispersed in the same liquid, between the solid–liquid interfaces of adjacent grains in contact; and (iii) the grain-boundary groove angle, ψ, formed between adjacent grains at the solid surface. It can be shown that these three angles are directly related to the energies of the interfaces that form them. If the angles are measured and the surface energy of the liquid, γ_{LV}, is known, then the energy of the interface between the solid and the liquid, γ_{SL}, and the grain boundary energy, γ_{SS}, as well as the surface energy of the solid, γ_{SV}, can be determined. The applicability of this method depends on the existence of a liquid which readily forms the relevant equilibrium angles but which does not react chemically with the solid. During investigations of several cemented carbide alloys, it has become apparent that the systems of certain carbides with liquid cobalt are suited to the measurement of the surface and interfacial energies by this method; the results of such measurements are presented in this communication.

Cemented carbides are alloys which consist of a carbide phase in combination with a metallic phase such as cobalt, nickel or iron. They are prepared by a process known as liquid-phase sintering, during which the metal is in the liquid state. It is now well established that the relative values of the interfacial energies have a considerable influence on the liquid-phase sintering process, and also on the appearance of the microstructure of the resulting alloys. The determination of these energies is therefore of specific as well as general interest.

Values of the interphase angles, θ and φ, for TiC, HfC, VC and NbC, with cobalt as the liquid phase, are given in Table 1. In all cases the angles were formed in a dynamic vacuum of between 10^{-6} and 10^{-5} torr. The angle of contact, θ, was determined by melting a small amount of cobalt on the polished surface of the polycrystalline carbide. The experimental technique has been described in detail[5,6]. For HfC and VC the values reported by Ramqvist[5] have been used. The measurements made in the present study for NbC and TiC were in good agreement with those of Ramqvist for the same carbides. The dihedral angle, φ, was measured from microsections of the sintered alloys, by measuring about one hundred apparent angles and taking the true value of φ as the median value of these[7,8].

It is to be noted that, for a given carbide, the values of θ and φ were not always measured at the same temperature. It has been found for several systems, however, that variations in temperature of this magnitude rarely affect the values of the angles significantly.

Table 1 Interphase Angles in Systems of Certain Carbides with Liquid Cobalt

Carbide	Angle of contact $\theta°$ at $T°$ C		Dihedral angle $\varphi°$ at $T°$ C	
TiC	26 ± 2	1,450	25 ± 2	1,450
HfC	$40 \pm 2*$	1,420	37.5 ± 2	1,500
VC	$13 \pm 2*$	1,420	8 ± 2	1,450
NbC	11.5 ± 1	1,500	16.5 ± 2	1,550

* Taken from ref. 5.

Table 2 Surface and Interfacial Energies of Systems of Certain Carbides with Liquid Cobalt

Carbide	Carbide grain boundary energy γ_{SS} (erg cm^{-2})	Carbide/cobalt interfacial energy γ_{SL} (erg cm^{-2})	Carbide surface energy γ_{SV} (erg cm^{-2})	Approximate temperature to which values apply (° C)
TiC	850 ± 200	440 ± 120	$2,135 \pm 150$	1,450
HfC	730 ± 200	385 ± 120	$1,825 \pm 150$	1,500
VC	925 ± 200	465 ± 120	$2,310 \pm 150$	1,450
NbC	930 ± 50	480 ± 50	$2,300 \pm 50$	1,550

The value of the groove angle, ψ, was determined for NbC on a polished, polycrystalline specimen, annealed for 10 h at 1,500° C *in vacuo*. Individual grooves were measured, using an optical interferometric technique very similar to that described by Hodkin et al. for UC (ref. 9), and the mean value of these was $156° \pm 2°$. Because of the formation of facets on the specimen surface during annealing, the number of undistorted grooves was small and consequently the accuracy of measurement was relatively poor. The above value of ψ yields a value for the ratio γ_{SS}/γ_{SV} of 0.41 ± 0.3 which is quite close to the values of between 0.36 and 0.41