our epoch and something of our nature. We do not know if the message will ever be found or decoded; but its inclusion on the Pioneer 10 spacecraft seems to us a hopeful symbol of a vigorous civilization on Earth.

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Note

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Superconductivity of Double Chalcogenides: $Li_xTi_{1.1}S_2$

Abstract. *Lithium titanium sulfides, $Li_xTi_{1.1}S_2$ ($0.1 < x \leq 0.3$), become superconducting over the temperature range from 10° to 13°K. They have the hexagonal Ti_3S_4 structure and should not be considered intercalation compounds. This is the first class of noncubic compounds with high transition temperatures.*

We here report the discovery of new superconducting compounds $Li_xTi_{1.1}S_2$ ($0.1 < x \leq 0.3$) whose properties are quite remarkable. After annealing at 600°C these compounds exhibit superconducting transition temperatures very much higher than those that have been reported in sulfides. Although none of the binary compounds of the constituents, Li-S, Li-Ti, or Ti-S, becomes superconducting above 1°K, the new ternary compounds do so over the temperature range from 10° to 13°K with "onset" temperatures as high as 15°K. The new compounds are also noteworthy in that such high transition temperatures are achieved for the first time in a hexagonal rather than cubic structure. It is also important to point out that the compounds with the composition $Li_xTi_{1.1}S_2$ are very unstable between 77°K and about 600°K.

When held for even a few hours at room temperature, the transition temperature drops a few degrees and the compounds no longer show a bulk effect. Subsequent annealing, however, completely restores the superconductivity as a bulk effect at the high transition temperatures mentioned above. These compounds can be prepared by melting together the appropriate amounts of Li metal and titanium sulfide, $Ti_{1.1}S_2$, having the CdI_2 structure. The double sulfides $Li_xTi_{1.1}S_2$ ($0.1 < x \leq 0.3$) have the hexagonal Ti_3S_4 structure. A comparison of the interplanar spacings and the observed intensities is given in Table 1 for $x = 0.3$.

Table 1. Crystal data for $Li_{0.3}Ti_{1.1}S_2$ (hexagonal structure, $a = 3.439 \pm 0.003$ Å, $c = 11.511 \pm 0.009$ Å); d, interplanar spacing; strong, s; medium, m; weak, w; very weak, vw; very very weak, vvw.

Intensity	*hkl*	d_{obs} (Å)	d_{calc} (Å)
m	002	5.772	5.756
w	100	2.961	2.978
w–m	004 101	2.887	2.883 2.878
s	102	2.642	2.645
m–s	103	2.351	2.353
w	104	2.070	2.069
vw	006	1.906	1.919
w	105	1.825	1.821
s	110	1.717	1.719
vw	112	1.646	1.648
w	106	1.615	1.613
vvw	201	1.480	1.477
w–m	202	1.441	1.442
w	203	1.387	1.388
vw	204	1.324	1.323
vvw	116	1.279	1.280
vw	205	1.250	1.250
vw	206	1.175	1.176
m	212	1.105	1.105
w	213	1.080	1.080
vw	214	1.048	1.048
vw	215	1.011	1.011
w	300	0.993	0.993
vw	216	.971	.971
w	220	.859	.860
w	312	.818	.818
vw	313	.808	.808

Many different phases exist in the Ti-S phase diagram, each one having a large homogeneity range (*1*). Titanium monosulfide, TiS, can crystallize with the NiAs structure, whereas the disulfide, TiS_2, crystallizes with the CdI_2 structure. Even though it is possible to bring about a continuous change from a NiAs structure to a CdI_2 structure, titanium sulfides with the composition $Ti_{1+x}S_2$ ($0.1 < x \leq 0.5$) have a different hexagonal structure (*2*). They belong to space group $P6_3mc$ with $a \simeq 3.42$ Å, $c \simeq 11.42$ Å, and two molecules per unit cell. The atoms are in the following positions: 2Ti(1) in special positions $2b$ ($\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z$) with $z \simeq \frac{3}{4}$; xTi(2) in $2b$ with $z \simeq 0$; 2S(1) in $2b$ with $z \simeq \frac{3}{8}$; and 2S(2) in the special positions $2a$ ($0, 0, z; 0, 0, \frac{1}{2} + z$) with $z = \frac{1}{8}$. The S atoms in $Ti_{1+x}S_2$ are in alternate hexagonal and cubic close-packing, whereas in both TiS and TiS_2 they are all hexagonal close packed. The Ti atoms occupy the octahedral sites in the close-packed array of the S atoms, in such a way that they form alternate completely filled and partly occupied sheets of metal atoms. The limiting composition is Ti_3S_4, because the partly filled sheets can only be half filled. The S octahedrons around the atoms forming the filled sheets share faces, perpendicular to the c axis, with the octahedrons of the partially filled sheets. There are two crystallographically independent S atoms in the structure. They have different environments: S(1) is at the center of a trigonal prism of Ti atoms, whereas S(2) is at the center of the octahedron. The compounds $Li_xTi_{1.1}S_2$ with $0.1 < x \leq 0.3$ crystallize with this structure. They do so because the ratio of metal to S is within the limit of existence for the sulfide $Ti_{1+x}S_2$ with $0.1 < x \leq 0.5$ and also because the effective radii of Li and Ti are nearly the same. It is not possible, on the basis of the x-ray data available at present, to determine which octahedral sites are occupied by the Li atoms. Neither before nor after annealing at 600°C did we find any evidence of superlattice reflections corresponding to a multiple a axis; therefore the metal atoms and the vacancies are not ordered in the half-filled layers. This disorder has also been reported for the titanium sulfides which have the same structure (*2*), whereas complete order has been shown to the exist for the isostructural Cr_2S_3 (*3*). Although we have not refined the structure of any of the $Li_xTi_{1.1}S_2$ compounds, we can estimate the metal-metal separation across the shared octahedral face to be approximately 2.88 Å for $x = 0.3$. The Ti-Ti distance in Ti metal is 2.90 Å; therefore some strong metal-metal bonding exists between the metal atoms sharing the octahedral faces. Furthermore, these values indicate that the compounds with the composition $Li_xTi_{1.1}S_2$ ($0.1 < x \leqq 0.3$) should be regarded as predominantly covalent compounds. In the corundum structure of Ti_2O_3, which can be regarded as an ionic compound, the Ti-Ti separation across the shared octahedral face is 2.58 Å (*4*).

A different phase exists for $Li_xTi_{1.1}S_2$ compounds with $0.5 < x < 1.5$. The x-ray powder patterns of these compounds do not resemble that of any titanium sulfide or that of $Li_xTi_{1.1}S_2$ ($0.1 < x \leqq 0.3$). For the compound with $0.5 < x < 1.0$, the x-ray pattern can be indexed on a tetragonal cell with $a = 4.97$ Å and $c = 5.93$ Å. We did not find any superconductivity above 1.12°K for any of these compounds. However, we did discover an incomplete superconducting transition at approximately 2°K for the compounds with $1.0 < x < 1.5$. In this case the x-ray pattern is similar to that of the compound for which $0.5 < x < 1.0$, but it contains extra lines indicative of yet another slightly different compound.

It is difficult at the present time to explain the high transition temperature for the compounds $Li_xTi_{1.1}S_2$ ($0.1 < x \leqq 0.3$). We can only state that, on the basis of the crystal chemistry of these compounds, they should not be regarded as intercalation compounds. Furthermore, in view of their superconductivity, these compounds do not seem to behave like intercalation compounds. The superconducting transition temperatures for this type of compounds range around 2°K. Recently Somoano and Rembaum (*5*) reported superconductivity in alkali-metal intercalation compounds of MoS_2. They found a superconducting transition temperature of approximately 1.3°K for Na_xMoS_2 and approximately 4.5°K for K_xMoS_2. After Rouxel *et al.* (*6*) reported the existence of K_xZrS_2, we found superconductivity, ranging from traces to a full bulk effect, in many other intercalation compounds, such as M_xZrS_2 and M_xHfS_2 with M = Na, K, Rb, or Cs. In these compounds the transition temperatures range between 1° and 3°K and are somewhat lower than in the corresponding MoS_2 phases. In almost all cases the transitions are partial and ill defined, and so no further effort was expended on these compounds. We have been unable to find superconductivity above 1.12°K in the corresponding compounds with TiS_2. The intercalation compounds were prepared by heating the constituents in a sealed silica tube to about 250°C and maintaining them at that temperature for several hours. It is thought that the compound $Li_xTi_{1.1}S_2$ with $x > 1.0$ is of an intercalated nature, because of its low transition temperature. But, if it is indeed an intercalation compound, it should be one of a new type of titanium sulfide.

In conclusion, we point out that these compounds constitute yet another example of high-temperature superconductivity at the expense of crystallographic stability (*7*). There is a large disparity in transition temperature between intercalation superconductors and three-dimensional systems. It is likely that many new superconductors with high transition temperatures exist, but these are not found because they are masked by their more stable and nonsuperconducting neighbors. This is the first time that such high transition temperatures have been observed in a hexagonal compound; all those that have been reported so far are cubic.

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Aftershocks Caused by Pore Fluid Flow?

Abstract. *Large shallow earthquakes can induce changes in the fluid pore pressure that are comparable to stress drops on faults. The subsequent redistribution of pore pressure as a result of fluid flow slowly decreases the strength of rock and may result in delayed fracture. The agreement between computed rates of decay and observed rates of aftershock activity suggests that this is an attractive mechanism for aftershocks.*

The frequency of occurrence of aftershocks following large shallow earthquakes decays with time. Typically the rate drops from thousands of aftershocks per day during the first day to 10 per day or less 100 days later. This decay requires a time-dependent process that is much faster than the large-scale tectonic loading and much slower than the propagation of elastic waves (*1*).

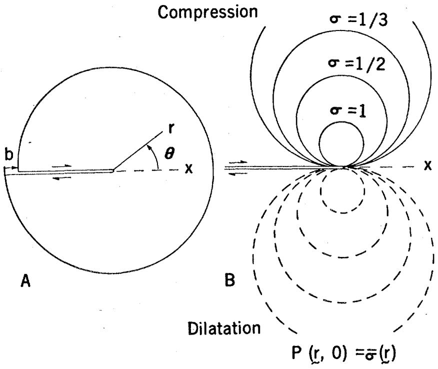

Fig. 1. (A) Representation of a fault's end by an edge dislocation with offset b; (B) the induced hydrostatic stress $\sigma(\mathbf{r})$. The initial pore pressure $P(\mathbf{r},0)$ is equal to $\sigma(\mathbf{r})$.

Theoretical and experimental investigations indicate that a viscous element is absolutely necessary in order to explain this time dependence of aftershock sequences. In model studies with friction and springs it has been impossible to produce aftershocks unless viscous dashpots are introduced. Similarly, computer models also require viscous elements to produce the necessary time-delayed event (*1, 2*). In other words, after a major earthquake there must exist some mechanism that "tells" a potential aftershock to wait before it occurs. Static fatigue is one possibility. However, its relevance to scales larger than laboratory samples has not yet been demonstrated. On the other hand, the decrease in the shear resistance of rocks in the laboratory with increasing fluid pore pressure has been well established, and its connection with earthquakes at Denver and Rangely, Colo-