10. The experimental plots were established on New York State forests near the locations named. The Russia stand was on Hartland loamy, very fine sand; at treatment it was 23 years old and averaged 9.4 m high with 1280 stems per hectare immediately after a thinning of about 10 percent. Plot size was 0.08 ha, with three replications. Foliar symptoms of K deficiency were slight. The North Lawrence stand was on Croghan loamy sand; it was 34 years old when treated and had an average basal area of 18.8 m^2/ha with 1430 stems per hectare 2 years after light thinning. Plot size was 0.12 ha with two replications.
11. North Lawrence samples were collected on 23 June 1976; Russia samples, on 25 September. The Rb and K in oven-dried foliage and litter samples were determined according to the method of A. A. R. Hafez, J. R. Brownell, and P. R. Stout [*Commun. Soil Sci. Plant Anal.* **4**, 333 (1973)], except that K rather than Cs was used to suppress interference in the Rb determintion by atomic absorption, and K was determined by flame spectrophotometry.
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Clustering Hypothesis of Some High-Temperature Superconductors

Abstract. *Cluster formation in metallic crystal lattices is important for most high-temperature superconductors.*

The concept of intermetallic bonding in inorganic compounds has been a favorite subject in materials science for many years. The existence of intermetallic bonding or metal-to-metal bonding leads to entirely new structures, particularly among the transition metal compounds. In these structures the metal-to-metal bonding manifests itself by the formation of clusters within the metallic lattice such as triangles, tetrahedra, octahedra, chains, and pairs (*1*). One of the first inorganic transition metal cluster compounds discovered was hydrated MoCl$_2$, whose structure contains octahedra of molybdenum atoms (*2*). Van Arkel (*3*) was one of the first to point out the importance of metal-to-metal bonding as a general phenomenon in the field of inorganic chemistry and used this concept as a perturbation to understand the stability of inorganic compounds. Metal-to-metal bonding was then discovered among numerous transition metal halides (*4, 5*) and resulted in a field of intensive study in organometallic chemistry (*6*).

In all these metal cluster compounds, whether they are typically ionic or organometallic, the metal-metal distance in the cluster—the intracluster distance—is about the same as that in the element. The distance between the clusters—the intercluster distance—varies greatly, depending on the type of compound involved, but is much larger than the metal-metal distance in the element. These intercluster distances have a strong impact on the physical properties of the compound. In the organometallic cluster compounds the distances between the clusters, which are pushed apart by the organic groups, are so large that the metal clusters show localized behavior. However, in numerous inorganic compounds such as the chalcogenides and phosphides, the intercluster distances, although larger than the distances in the metal, can still be metallic distances, resulting in metallic conductivity.

Table 1. Intra- and intercluster distances (Me-Me$_{IA}$ and Me-Me$_{IR}$, respectively) in some high-T$_c$ superconducting (SC) and nonsuperconducting (NSC) cluster compounds.

Compound	Me-Me$_{IA}$ (Å)	Metallic Me-Me$_{IR}$ (Å)	Type and dimensionality of metallic cluster lattice	Nonmetallic Me-Me$_{IR}$ (Å)	Element Me-Me (Å)	Electrical properties
MoN	2.67	3.00	Triangles, three-dimensional		2.73	Metallic, SC
Nb$_3$Sn	2.64	3.24	Chains, three-dimensional		2.86	Metallic, SC
PbMo$_6$S$_8$	2.57–2.74	3.26	Octahedra, three-dimensional		2.73	Metallic, SC
YRh$_4$B$_4$	2.63–2.75	3.14	Sheets of tetrahedra, three-dimensional		2.69	Metallic, SC
Mo$_2$S$_3$	2.85–2.87	3.22	Zigzag chains, two-dimensional	4.10	2.73	Metallic, NSC
VMo$_2$S$_4$	~2.85	~3.28	Zigzag chains, two-dimensional	~4.00	2.73	Metallic, NSC
Ga$_x$Mo$_2$S$_4$	2.84		Tetrahedra, isolated	4.05	2.73	Semiconducting, ferromagnetic
ReSe$_2$	2.65–2.93	3.08	Planar Re$_4$ groups, one-dimensional	3.92–4.12	2.76	Semiconducting, diamagnetic

This cluster hypothesis of short and also long (but still metallic) distances now appears to be an important feature for a number of superconducting structures with high transition temperatures (T_c's). It is not altogether a new idea and had been pointed out previously for one structure or another (*7*). The systematic occurrence of metal clustering in high-T_c superconducting compounds, however, was first observed in the ternary sulfides MeMo$_6$S$_8$ (where Me stands for tin, lead, and so on) (*8*); molybdenum clusters into octahedra with short distances of ~ 2.70 Å and intercluster but still metallic distances of 3.26 Å, about 16 percent larger than that in the element. We then observed that similar clustering of the metal lattice occurs in other high-T_c superconductors such as hexagonal MoN (*7*) and the cubic β-tungsten or A-15–type compounds. In MoN three of every four molybdenum atoms cluster into triangles (Fig. 1), and in the A-15 phases the metal atoms, such as niobium, cluster into chains with long but still metallic distances between the clusters (Table 1). The recently discovered new series of high-T_c superconducting compounds MeRh$_4$B$_4$ (where Me is a transition or rare earth element) is another example of their clustering behavior (*9, 10*). In this structure the rhodium atoms cluster into sheets of tetrahedra with a distance of ~ 2.70 Å; the sheets are interconnected through a long but still metallic distance of 3.14 Å (Fig. 2). The high-T_c superconducting materials (Th, RE)$_2$C$_3$ (where RE is a rare earth element) crystallize in the body-centered Pu$_2$C$_3$-type structure (*11*). No clearly separated clusters occur in this structure, but the metal lattice does distort into a lattice of shorter (3.35 Å) and longer (3.70 Å) metallic distances. It is difficult to state whether there is direct metal-metal bonding between plutonium atoms.

In all these superconducting structures with high transition temperatures an essentially three-dimensional metal lattice is maintained, the metal-metal distances

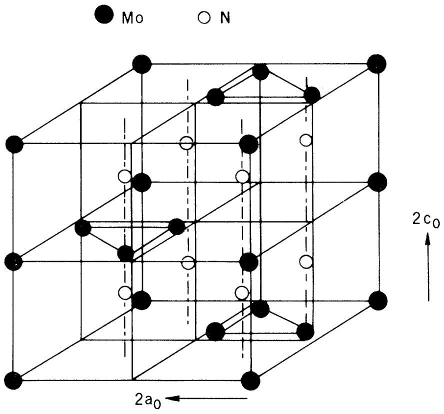

Fig. 1. Triangular clusters of molybdenum in hexagonal MoN.

varying from short ones within the clusters to distances 12 to 20 percent larger than in the metal between the clusters (Table 1). In metallic cluster compounds such as Mo_2S_3 (*12*) and VMo_2S_4 (*13*) the molybdenum atoms form chains. They are not superconducting because a three-dimensional metal lattice between the chains is no longer maintained. Other interesting examples of nonmetallic cluster compounds are the spinels $Al_xMo_2S_4$ and $Ga_xMo_2S_4$ (*14, 15*) and ReS_2 and $ReSe_2$, which have a distorted $Cd(OH)_2$-type structure (*16, 17*). In the spinels the molybdenum atoms cluster into tetrahedra. The distances between these clusters are so large that they are no longer intermetallic ones (Table 1). The molybdenum spinels are therefore semiconducting and ferromagnetic, because of the unpaired electron localized on each tetrahedral molybdenum cluster (Fig. 3). In ReS_2 and $ReSe_2$ the rhenium atoms form Re_4 clusters, which are linked to chains with a still metallic intercluster distance of 3.08 Å. The chains are too far apart to form a three-dimensional metallic lattice. The compounds are diamagnetic.

Some of the recently discovered ternary borides $MeRh_4B_4$ (where Me is a rare earth) (*9*) are also magnetic. However, the rhodium lattice is metallic and the magnetism is caused by the effective magnetic moment of the rare earth ions, which for gadolinium, terbium, dysprosium, and holmium is large enough to render the compounds magnetic. It is also quite interesting that for the corresponding series $MeCo_4B_4$ (*18*) and $MeRh_4B_4$ the ratio of unit cell axial lengths c/a varies in the same way and covers the very narrow range of 1.39 to 1.41. However, for a value of $c/a > 1.398$ the cobalt compounds do not exist (*18*), whereas the rhodium compounds do exist, such as for Me = neodymium, samarium, and thorium (*10*). At the same time their superconducting transition temperatures drop considerably, indicating that the superconductivity is strongly related to the c/a ratio and the corresponding intercluster Rh-Rh distances. The distances and electrical properties are listed in Table 1. On an empirical basis we distinguish three types of distances in these cluster compounds. The short intracluster distance is as much as 8 percent smaller than in the element. The long but still metallic intercluster distance is 12 to 20 percent larger than in the element. The nonmetallic intercluster distance is at least 30 percent larger than in the element. All the distances listed are nearest-neighbor ones.

The clustering of the metal lattice is a characteristic of all high-T_c superconductors so far discussed. As the metal lattice breaks up into clusters, it is essential that a three-dimensional metal lattice is maintained with long intercluster distances about 12 to 20 percent larger than in the metal. The metal lattice is, in a sense, destabilized by clustering, and this crystallographic instability is closely connected with the high-T_c superconductivity. The metallic intercluster distance seems to be an essential parameter in these superconductors, but a few factors such as the type of cluster and number and size of the anions are also of importance. For $MeMo_6S_8$ (Me = tin, lead, and so on) a critical intercluster distance of 3.26 Å was proposed (*19*). This might well be true within the series of ternary sulfides, but some of the rare earth molybdenum selenides (*20*) such as $LaMo_6Se_8$ have high T_c's (up to 12°K). The intercluster distances here are larger than in the corresponding sulfides because the selenium atoms expand the lattice considerably. Since the selenium compounds are more covalent and therefore create a lower charge on the molybdenum atoms, the critical and metallic intercluster distance is larger. For that reason, metal ions larger than lead or tin are needed to obtain this optimal distance, and in the case of the selenides these are the rare earth ions. Although the intercluster distance is larger than in the sulfides, it is still a metallic distance because of the stronger covalency effect.

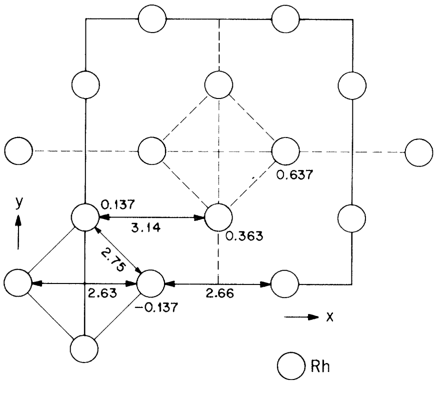

Fig. 2. Projection of the Rh_4 tetrahedra along the [001] direction. The heights of the rhodium atoms and intermetallic distances are indicated.

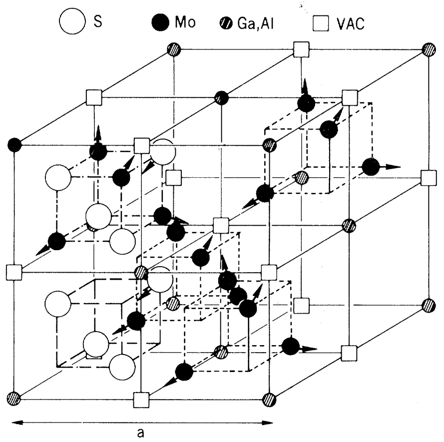

Fig. 3. Tetrahedral clusters of molybdenum around vacancies in the spinels $Al_{0.5}Mo_2S_4$ and $Ga_{0.5}Mo_2S_4$. Shifts of the molybdenum atoms are indicated by arrows.

The clustering hypothesis described above is seen to add considerably to the systematic understanding of superconductivity in a number of compounds. However, in its present form the hypothesis does not apply to all high-T_c superconductors. For instance, no clustering is observed in superconductors such as niobium nitride and palladium hydride. They have the sodium chloride structure, and the nearest-neighbor metallic distances are invariably all longer than in the metal. Clustering of the metal lattice is not necessarily a condition for all high-T_c superconductivity, but in a number of high-T_c superconducting structures it is an interesting aspect of their crystallography. Its study may lead to an improved understanding of the crystallographic stability of these structures.

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Folate Conjugase: Two Separate Activities in Human Jejunum

Abstract. *Previous perfusion studies of the human jejunum suggested that conjugated folate is hydrolyzed on the mucosal surface. The techniques of cell fractionation and DEAE and gel chromatography led to the identification of two separate folate conjugase activities in human jejunal mucosa: one membrane-bound and concentrated in the brush border, the other soluble and intracellular. These enzyme activities exhibit different* pH *optima, molecular weights, and inhibition characteristics. Folate conjugase in the brush border may accomplish the initial digestion of dietary pteroylpolyglutamates.*

The intestinal absorption of dietary folate requires hydrolysis of the predominant pteroylpolyglutamate forms to pteroylmonoglutamate (*1*). The hydrolytic enzyme, a γ-glutamyl hydrolase referred to as folate conjugase, is concentrated in the mucosa of the small intestine (*2*). The cellular location of this enzyme, and hence the sequence of folate digestion and membrane transport, is poorly understood. If mucosal folate conjugase is primarily lysosomal as reported (*3*), then pteroylpolyglutamates should enter the epithelial cell prior to hydrolysis. In contrast, the observation that perfusion of the human jejunum with ^{14}C-labeled pteroylheptaglutamate results in the appearance of its hydrolytic products in the intestinal lumen suggests that surface hydrolysis of pteroylpolyglutamates precedes cellular entry (*4*). We report evidence for two separate folate conjugase activities in human jejunal mucosa: one soluble and intracellular, and the other membrane-bound and concentrated in the brush border.

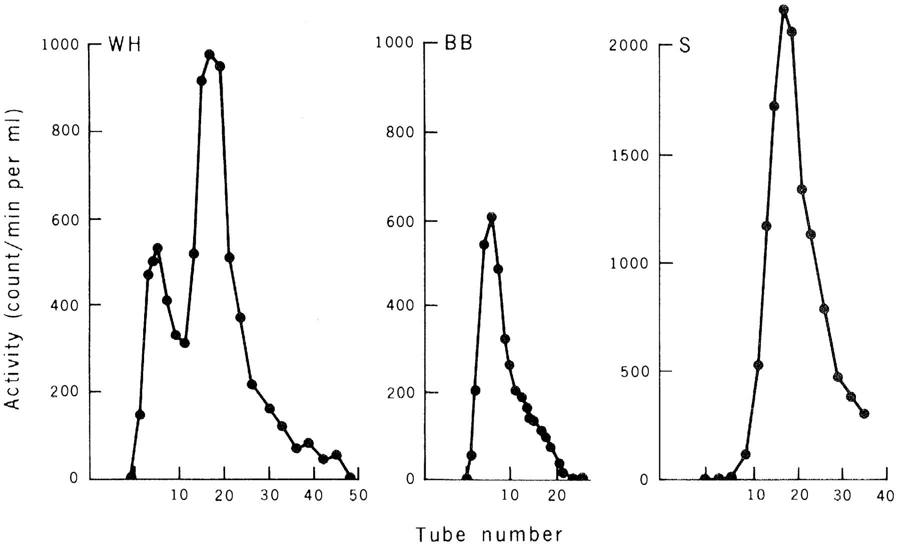

Fig. 1. Folate conjugase activity at *p*H 4.5 in human jejunal mucosal fractions after solubilization with Triton X-100 and passage through DEAE-cellulose and Sephadex G-200. Peaks 1 and 2 of the whole homogenate (WH, left panel) correspond in elution volume to peaks obtained after separate treatment of brush border (BB, center panel) and intracellular supernatant (S, right panel) fractions. Approximate molecular weights are: peak 1 (BB) 91,000, and peak 2 (S) 45,000. Subsequently, peak 1 (BB) was found optimally active at *p*H 7.5 and not inhibited by PHMB, while peak 2 (S) was optimally active at *p*H 4.5 and completely inhibited by PHMB.

Segments of human jejunum were obtained at surgery from obese patients undergoing elective jejuno-ileal bypass. The mucosa was dissected from the remainder of the jejunal tissue, frozen immediately, and stored at −70°C until use. We fractionated the tissue by a modification of the method of Schmitz *et al.* (*5*). In a Waring Blendor, a 1 percent homogenate of mucosa was prepared in 50 m*M* mannitol, 2 m*M* tris (*p*H 7.1) at 5°C and filtered, yielding a whole homogenate fraction (WH). Calcium chloride was added to the homogenate to a final molarity of 10 m*M*. The mixture was stirred for 10 minutes and centrifuged at 2000*g* for 10 minutes, producing a "cell debris" precipitate (fraction P_1). Centrifugation of the supernatant at 20,000*g* for 15 minutes resulted in a second pellet which was washed twice to give a brush border fraction (BB) in which membrane particles could be identified by electron microscopy. The supernatant was further centrifuged at 50,000*g* for 2 hours, resulting in a final pellet (fraction P_3) and a final supernatant (fraction S). Each pellet was resuspended in the mannitol-tris buffer before assay. All fractions were assayed for protein (*6*), sucrase (*7*), and folate conjugase.

Folate conjugase activity was assayed with the use of a synthetic pteroyltriglutamate, pteroyldi-γ-[^{14}C]glutamate as the substrate, and the charcoal precipitation method (*8*). On the basis of a preliminary kinetic study with whole homogenates showing linear enzyme activity with respect to incubation time and enzyme concentration and zero order kinetics at concentrations greater than 6.5 μ*M*, we chose a substrate concentration of 13 μ*M* and a reaction time of 15 minutes. An initial experiment indicated that folate conjugase activity in fraction S was maximal at *p*H 4.5 while the enzyme in fraction BB was active over a broad *p*H range, with major activity at *p*H 7.5.

The results of six fractionation experiments are shown in Table 1. Fractions P_1 (cell debris) and S (final intracellular supernatant) accounted for 96 percent of the total protein. Sucrase, a brush border marker enzyme, was distributed nearly equally in the P_1 and BB fractions, while its specific activity was concentrated 12-fold in BB. At *p*H 4.5, 73 percent of folate conjugase was found in S while, at *p*H 7.5, the enzyme was distributed among P_1, BB, and S, with 12 percent recovery in BB. The specific activity of folate conjugase in S was eight times greater at *p*H 4.5 than at *p*H 7.5, but similar at