netically determined transition at $\sim 2.1°K$ for this pressure is associated with bulk superconductivity. We believe, on the basis of our model (see below), that all the magnetically observed transitions at pressures above about 3 kbar are associated with bulk superconductivity and await specific-heat measurements at these pressures to test whether this is correct or not. The upper limit of 0.1°K imposed upon the T_c of α-U at zero pressure by the specific-heat measurements,[11] coupled with the specific-heat measurements at 10 kbar,[12] clearly indicates the sensitivity of the T_c of α-U to pressure below 10 kbar.

An examination of Fig. 3 shows a marked change in the pressure dependence of T_c above 10 kbar. Thus, following the initial rapid increase (by more than an order of magnitude) T_c levels off at about 2.1°K above 9 kbar. These results confirm the decrease in $\partial T_c/\partial P$ with increasing pressure suspected from the trend of the earlier measurements.[1] T_c then remains essentially pressure independent between 9 and 13 kbar, and then decreases slowly as the pressure is increased further. The rate at which T_c decreases is obscured by a gradual, but considerable broadening of the transition at pressures above 15 kbar. This may be an indication of increasing pressure inhomogeneity within the sample, possibly due to the deformation of the cylinder walls. However, there was no evidence for such behavior in the transition of the tin manometer since its width remained essentially constant over the entire pressure range. Furthermore, the transition width decreased upon reducing the pressure so that the cause of the broadening appeared to be quite reversible.

In view of the upper limit of 0.1°K on any possible transition to the bulk superconducting state we shall consider α-U to be nonsuperconducting at zero pressure. The following considerations, however, will not be appreciably affected in the event that α-U is found to be a bulk superconductor at a temperature lower than 0.1°K. Now any discussion of the superconducting properties of α-U has to explain the three main features of the T_c-pressure curve: (i) the pressure-induced superconductivity, (ii) the initial, abnormally rapid, increase of T_c with pressure—namely a rise from 0 to 2°K for an applied pressure of ~ 9 kbar, which corresponds to a volume decrease of less than 1%, (iii) the broad maximum in T_c, centered about 11 kbar, followed by a relatively slow decrease of T_c with further application of pressure.

Other known systems showing pressure-induced superconductivity are the semimetal bismuth,[27] the semiconducting elements Te,[28] Sb,[29], Si,[30] Se,[31] and Ge,[30] and

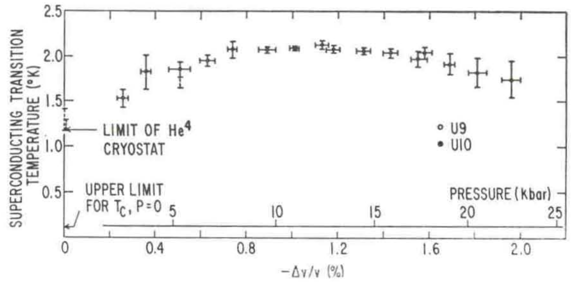

FIG. 3. Superconducting transition temperature of α-uranium as a function of % change of volume.

a number of semiconducting compounds[32] all of which become superconductors following a pressure-induced transformation, with an associated decrease in volume, to a metallic phase. However, neither resistivity nor compressibility measurements on α-U as a function of pressure at room temperature indicate the occurrence of a phase change. It is possible that such a phase change takes place below room temperature, but we think this is unlikely. Thus the possibility arises that α-U may be the first pressure-induced superconductor which does not undergo a first-order crystallographic transition to the superconducting phase.

The second feature of the T_c–P curve, the initial rapid increase of T_c with pressure, is peculiar to pure α-U since it has not been observed in α-, β-, and γ-uranium alloys. This change on alloying contrasts strongly with the behavior of lanthanum-rich solid solutions[23] with Y, Th, Yb, Pr and Gd (but not Ce) which retain the rapid increase of T_c with pressure observed in pure La. This suggests that the cause of the initial rapid increase of T_c with pressure in α-U is due to a weak electronic transformation. Such a transformation has been postulated by Fisher and McSkimin[33] to account for an anomaly at 43°K in their elastic-constant data and anomalies which have been observed by a number of workers in several other properties of α-U, such as Hall constant,[34] resistivity[34] and thermal conductivity[35] at this temperature. However, there does not appear to be any anomaly in the magnetic susceptibility in the region of 43°K[36] (Fig. 4). X-ray and neutron diffraction measurements[18] subsequently showed that although there is no crystallographic phase transformation at 43°K there is, however, a change in the temperature dependence of the atomic position parameter and that there is also an increase in volume amounting to some 0.2% between 50 and 4.2°K. In addition extra reflections were observed in the neutron pattern

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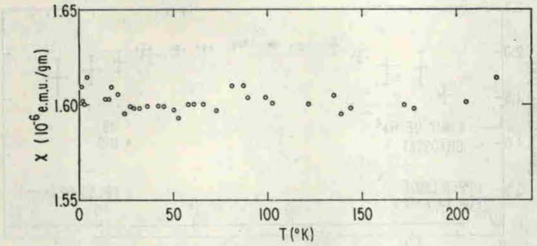

FIG. 4. The magnetic susceptibility of α-U from 1–200°K. The value observed at 297°K was $1.645\pm0.030\times10^{-6}$ emu/gm.

which were tentatively ascribed to a magnetic contribution. However, these extra reflections were also present at room temperature and therefore cannot be associated immediately with the "43°K transformation."

We propose, for convenience, to label the phase of α-U below 43°K at atmospheric pressure as α_0. Since there is an increase in volume with decrease of temperature below the $\alpha\rightarrow\alpha_0$ transformation it is not unreasonable to suppose that the effect of pressure would be to inhibit the formation of the α_0 phase. We propose therefore to associate superconductivity with the α-U phase, but not with the α_0-U phase. We can now describe the superconducting behavior of uranium at zero pressure since the grains are in the nonsuperconducting α_0 phase, whereas the grain boundaries, because of the associated strains introduced upon cooling, behave like the α phase and are responsible for the filamentary superconductivity. This description calls for an $\alpha-\alpha_0$ phase boundary which is strongly depressed in temperature by the application of a few kbar pressure. A study of the effect of pressure upon any of the anomalies observed in the physical properties of α-U at 43°K would be of considerable interest and would provide a positive test of this explanation. Though Geballe *et al.*[9] have also suggested this explanation for transitions observed below 0.8°K we differ from them in believing that the entire superconducting behavior of uranium may be accounted for by this model, rather than a combination of two explanations such as they adopted.

We should first like to consider one possible picture for this "43°K transformation" as suggested by Geballe *et al.*,[9] but which we shall express slightly differently. Namely, that an electron transfer takes place at 43°K from a $5f6d7s$ conduction band to a virtual bound (vb) state[37] constructed from the $5f$ conduction-electron wave functions. We shall assume that such a vb state just overlaps the Fermi level and we associate an increase in its population with an upward movement of the Fermi level, relative to the bottom of the vb state, as the volume increases below 43°K. Such a vb state could be either magnetic (m) or nonmagnetic (nm).

In order to estimate the effect of populating vb states we shall consider some examples of known behavior. Unfortunately, it is impossible to consider a nmvb state involving $4f$ electrons since vb states involving such electrons are usually well localized and carry a magnetic moment,[38] so we are obliged to compare the relative behaviors of magnetic and nonmagnetic $3d$ vb states. The addition of 1 at% Fe to V to form a nmvb state[39] lowers T_c by ~1°K.[40] However, this decrease in T_c is consistent with the "valence effect"[41] (the systematic variation of T_c with electron concentration across the transition series) and does not require that the actual presence of the nmvb state contributes to the lowering of T_c. In fact, since scattering from a nmvb state does not destroy the time-reversal invariance of the electron wave functions, there is no reason to expect that such scattering would decrease T_c.[42] Thus unless the formation of a nmvb state in α_0-U can be considered to alter the effective valence we would not expect such a state to change T_c markedly.

Magnetic vb states, on the other hand, play an active role in reducing the value of T_c. For example Fe dissolved in Mo[43] reduced T_c at a rate of 60–80°K per at%.[44] However, should a mvb state with a moment as small as $10^{-2}\ \mu_B$ form in U below 43°K and produce paramagnetic behavior there would be a temperature dependence of the susceptibility which would result in an increase of about 5% between 40 and 1°K. As no such temperature dependence of the susceptibility is observed (Fig. 4), this model is only appropriate if the extra postulate is made that the mvb states order antiferromagnetically as they form.

We should like to offer an alternative explanation for the behavior of α-U in terms of the formation of a spin-density wave (SDW)[45] at 43°K which opposes the superconductivity of α_0-U. The creation of a SDW scarcely affects the magnetic susceptibility,[46] but does reveal itself in anomalies in other physical properties such as Young's modulus,[47] resistivity,[47,48] Hall coefficient,[48] and thermal expansion[47,49]—anomalies which are also observed in α-U at 43°K. We then suggest that the application of pressure destroys the SDW, as is

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