the anomaly is quite different: H_{hf} *decreases* steeply with T and around $T/T_c \cong 0.5$ it even changes sign. But it must be pointed out that the sign of H_{hf}(Sn*Co*) is *negative* (~−22 kOe) while that of H_{hf}(Ge*Co*) is *positive* (~+46 kOe); the sign crossover is slightly shifted in phase in the two series for a Co host (see inset in Fig. 2). Thus one might expect an anomaly similar to H_{hf}(Sn*Co*) rather for Ga in Co and our data do indeed bear this out qualitatively. $H_{hf}(T)$ in Ga*Co* decreases rapidly although less steeply than for Sn. Thus Ga and Ge with hyperfine fields of opposite signs display strong anomalies which appear to be complementary to each other. In the case of As which has a large positive field (~+275 kOe), $H_{hf}(T)$ shows close scaling with $\sigma(T)/\sigma(0)$ up to $T/T \cong 0.5$ where the hcp → fcc phase transition occurs. At this point, however, there is a discontinuity and H_{hf} abruptly seems to scale with a normalization quite different from that of the fcc host magnetization. A discontinuity at the same point is observed also for $H_{hf}(T)$ in Ga*Co*. $H_{hf}(T)$ in Ge*Co* shows no discontinuity within experimental errors but does attain a maximum at this temperature.

Anomalies of the types reported here, together with that for Sn, *occur only in a Co host*;[8] they appear to be related to each other and occur systematically at well-defined elements in the 4*sp* and 5*sp* series. These clues, especially the latter, might indicate that their origin is connected intimately with the basic feature of these hyperfine fields, namely, the competition of the different contributive interactions. This special set of temperature anomalies of the hyperfine fields of *sp* elements at the points of sign crossover presents many distinctive features, which may provide for the first time sufficiently compelling criteria for a unique and common theory for these effects. It is to be hoped that this would lead to new knowledge especially about the origin of positive hyperfine fields which have been the subject of much debate.

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New Sequence of Structural Phase Transitions in Na_xWO_3

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Using precise lattice-parameter measurements, "cubic" Na_xWO_3 ($0.62 \leqslant x \leqslant 0.94$) has been found to transform from the ideal perovskite structure to three other related forms. The transition sequence is described in terms of a single vectorlike order parameter involving static in-phase tilts of WO_6 octahedra and is the zone-boundary analog of the ferroelectric series of transitions in $BaTiO_3$, the [001] tilt component arising from the condensation of the M_3 mode. Unexplained features of structural and Raman studies can now be interpreted.

The nonstoichiometric compounds Na_xWO_3 have recently attracted much attention because of their unusual electronic-transport properties. Of particular interest are the metal-nonmetal transition at $x \approx 0.2$,[1] the enhancement of the superconducting properties[2] around this composition, and the large concentration-dependent Kohn anomaly[3] reported for $0.56 < x < 0.83$. It is evident from these studies that structural considerations, via strong electron-phonon interactions, play a substantial role in determining the detailed transport behavior. In view of this, I have carried out a precise x-ray study in order to understand the structural aspects of Na_xWO_3 ($0.62 \leq x \leq 0.94$). The results show that is is not always correct to assume, as is usual in the literature, that the compounds in this composition range are cubic. In fact, I find that, for x in this range, Na_xWO_3 can exist in four distinct forms at various temperatures, only one of them being the undistorted cubic perovskite structure. Furthermore, the sequence of transitions between the four phases is one which has been predicted to occur in perovskites on thermodynamic and group-theoretical grounds[4] but has not, until now, been observed.

Although it has been known for some time, from birefringence[5] and x-ray[6] measurements, that Na_xWO_3 ($x \geq 0.5$) has a slightly distorted form of the ideal perovskite structure at room temperature, the details of the structure have remained obscure. In the present experiments I have measured the lattice parameters of Na_xWO_3 as a function of temperature for three values of x (0.62, 0.81, and 0.94 ± 0.01). From the temperature dependence of the lattice parameters and a knowledge of the possible modes of structural modification of perovskites, I have been able to elucidate the structural behavior and the mechanism leading to the observed sequence of transitions.

The lattice parameters of electrolytically grown crystals (from the same batch as the crystals used in the Raman study by Flynn, Solin, and Shanks[7]) were recorded continuously as a function of temperature using a very sensitive x-ray backscattering technique[8] and the results are shown in Fig. 1 for a crystal with $x = 0.81$. On cooling, the crystal is seen to pass through two distinct anisotropic phases before transforming to a cubic phase which persists down to at least -180°C. Note that my observation of a return to isotropic symmetry at low temperatures is consistent with the findings of Ingold and De Vries.[5] The low-temperature cubic phase, however, is not the ideal perovskite structure (as evidenced by weak superlattice reflections and by the existence of first-order Raman scattering[7] which disappears only at the uppermost transition); assuming that the W ion is not displaced and that the only structural distortions arise from the tilting of regular[9] WO_6 octahedra, I assign the space group $Im3$ (T_h^5), with $z = 8$, to the low-temperature cubic phase as this describes the only one of 23 possible tilt arrangements listed by Glazer[10] [apart from the ideal perovskite structure, space group $Pm3m$ (O_h^1), with $z = 1$] which is consistent with cubic symmetry. The tilting of this phase can be summarized, using

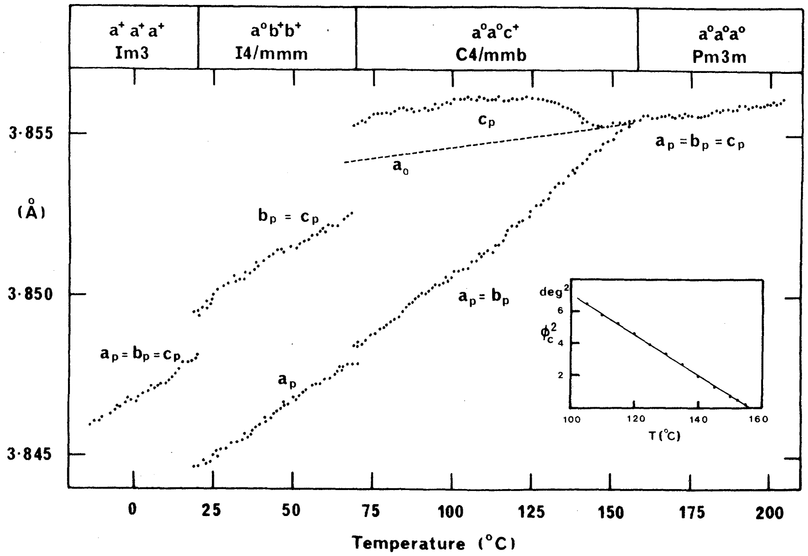

FIG. 1. Pseudocubic subcell spacings a_p, b_p, c_p for a crystal of $Na_{0.81}WO_3$. a_0 (broken line) is the extrapolation of a_p from the cubic phase. The spacings are calculated from the positions of the {113} reflections at $\theta > 82°$. Inset: Square of the octahedron tilt angle, φ_c^2, for the same crystal.

Glazer's notation,[10] as $a^+a^+a^+$, which describes a perovskite structure having equal octahedron tilts about each of the three pseudocubic axes, denoted by a_p, b_p, and c_p. The + superscript signifies that the tilts *about* a particular axis are in the same sense *along* that axis. In the $a^+a^+a^+$ phase, the effect of the tilting is to double each of the cell spacings so that now $a = 2a_p = 2b_p = 2c_p$ and the space group $Im3$ is referred to these doubled axes. Weak $\{310\}$ and $\{321\}$ superlattice reflections, observed on long-exposure Debye-Scherrer x-ray photographs, are consistent with this assignment. If we now assume that one of the tilt components is lost at each transition (as is the case in most transitions involving more than one tilt component, including[10] the uppermost transitions of $NaNbO_3$) we can describe the lower anisotropic phase as $a^0b^+b^+$ (i.e., zero tilt about a_p and two equal tilts about b_p and c_p). This phase will be tetragonal $[I4/mmm\ (D_{4h}{}^{17})]$ with $z = 8$ and $a > c$, as I have observed experimentally; now, $c = 2a_p$; $a = 2b_p = 2c_p$. Similarly, we can describe the upper anisotropic phase by $a^0a^0c^+$ which will be face-centered tetragonal $[C4/mmb\ (D_{4h}{}^5)$, $z = 4$ referred to unit cell axes $c = c_p$; $a = 2a_p = 2b_p]$ with $2c > a$, only the tilt component about c_p remaining: In Fig. 1 this is reflected by the virtual temperature independence of c_p in this phase. Finally, the remaining tilt component is lost to give the ideal perovskite structure with $a^0a^0a^0$. A partial phase diagram for Na_xWO_3 is shown in Fig. 2 and this is in reasonable agreement with the findings of other studies shown for comparison in the same figure. However, the line separating the two tetragonal phases, which is crucial to an understanding of the sequence of phases, has not been observed before although it became evident in a reexamination of the Raman data of Flynn, Solin, and Shanks[7] shown in Fig. 2.

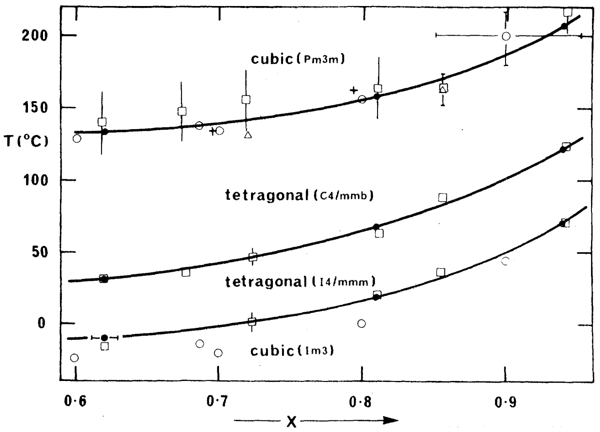

FIG. 2. Phase diagram for Na_xWO_3. ●, this work; ○, Ingold and De Vries (Ref. 5) (birefringence); △, Bonera *et al.* (Ref. 16) (NMR); +, Inaba and Naito (Ref. 12) (specific heat); □, Flynn *et al.*, (Ref. 7) (Raman scattering).

We now consider some of the physical implications of this scheme of structural transitions. Firstly, to the uppermost tetragonal phase one can assign a single static order parameter, φ_c, the tilt angle of the octahedra about $c_p[001]$. On cooling, the direction of the resultant tilt axis changes to $[011]$ at the tetragonal-tetragonal transition, and then to $\langle 111 \rangle$ in the low-temperature cubic phase, i.e., the transition sequence is described by a single, three-dimensional order parameter $(\varphi_a, \varphi_b, \varphi_c)$ transforming like an axial vector. At the uppermost transition the component φ_c is induced by the condensation of a soft mode at the zone boundary, $q = (\frac{1}{2}, \frac{1}{2}, 0)2\pi/a_p$ $(M_3$, describing in-phase librations of WO_6 octahedra about $c_p)$. The remaining transitions (of first order, see below) are associated with the reorientation of the order-parameter vector. In this respect the sequence is thermodynamically analogous to that occurring in the well-known ferroelectric, $BaTiO_3$, where the order parameter involved is a spontaneous polarization. The essential difference between these sequences lies in the wave vector of the soft mode as discussed by Vinberg *et al.*[4] Secondly, the $a^+a^+a^+$ structure, isomorphous with that of $D_{0.53}WO_3$,[11] is very rarely encountered: I believe that the metallic character of these perovskites is responsible in that the electron gas would favor an isotropic structure and would also tend to screen long-range Coulombic forces which might otherwise have led to the cooperative displacement of W ions, as is the case in many nonconducting perovskites.

In the $a^0a^0c^+$ phase, the order parameter, φ_c, may be calculated assuming rigid octahedra with no distortions,[9] from $\varphi_c = \cos^{-1}(a_p/a_0)$, where a_0 is the extrapolated cubic cell spacing, as shown in Fig. 1. The inset of Fig. 1 shows that φ_c is continuous at the uppermost transition within the experimental resolution, in agreement with the specific heat data of Inaba and Naito.[12] We note that $D_{4h}{}^5$ and $D_{4h}{}^{17}$ are both subgroups of $O_h{}^1$ permitting continuous transitions from $O_h{}^1$ to either of these groups.[4] However, according to the same considerations, it is not possible to pass continuously from $D_{4h}{}^5$ to $D_{4h}{}^{17}$ or from $D_{4h}{}^{17}$ to $T_h{}^5$ and these transitions are necessarily of first order, as observed experimentally.

We may compare the behavior of Na_xWO_3 at the uppermost transition with the structural transition in $SrTiO_3$ which is associated with an identical order parameter, except that in this case the tilts are described by $a^0a^0c^-$ [adjacent (001) layers of TiO_6 octahedra rotate in antiphase]. One would therefore expect $SrTiO_3$ and Na_xWO_3 to exhibit the same critical exponent, β. For $SrTiO_3$ within the reduced temperature range $t \equiv (T_c - T)/T_c \leqslant 0.05$, β has values[13] around 0.35 appropriate to either a Heisenberg or an $n = 1$ or 2 Ising model depending on the external stress conditions. Outside this range, β crosses over to the mean-field value of 0.50. Referring to the inset of Fig. 1, it is found that $\varphi_c \sim t^\beta$ with $\beta = 0.50 \pm 0.03$ at least within the range $0.01 \leqslant t \leqslant 0.13$, in agreement with the NMR measurements of Borsa.[14] It appears, therefore, that the critical region is considerably narrower than in $SrTiO_3$. We note that the above equation for φ_c is valid only in the absence of critical fluctuations and hence other techniques, which measure φ_c directly, will be required to probe any critical behavior.

The description of the structural behavior of Na_xWO_3 above may now be used to interpret unexplained features observed in several studies, particularly neutron-scattering,[9] x-ray,[15] and NMR[16] experiments. The mechanism of the phase transition sequence presented here, in terms of the condensation of an M_3 zone-boundary mode followed by reorientation of the order-parameter vector, is also completely compatible with the Raman scattering results of Flynn, Solin, and Shanks.[7] Moreover, these authors show that no alternative space-group assignments would be consistent with their data.

A room-temperature neutron study[9] of powder Na_xWO_3 ($x = 0.54$[17] and 0.73) has been attempted and superlattice reflections were observed which are consistent with the conditions imposed by the space group we have assigned to these compositions. With the present availability of large, high-quality crystals of Na_xWO_3, it would be useful to carry out a full neutron study, firstly to check that the superlattice reflections occurring in the other phases are consistent with the proposed structures, and secondly to complement the lattice dynamical information already obtained from Raman scattering.

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