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Ternary transition-metal aluminide alloy formation: The BiF_3 structure

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Almost 50 ternary transition-metal aluminides have been reported in the ordered BiF_3 structure, representing roughly half of the observed ordered ternaries. To investigate the possible occurrence of other aluminides in this structure, the heats of formation of 38 ordered M_2NAl ternaries, most not reported to occur, have been calculated. While all but one is stable relative to the elemental metals, the test for ternary stability requires comparison of the ternary heat with competing two and three phase mixtures of binary phases. Of the BiF_3 ternaries hitherto unreported, nine are estimated to occur while eighteen are found to be unstable. The pattern of occurrence obtained from experiments and calculations taken together suggests that on the order of another 20 compounds beyond those predicted here could exist. Thus, this important ordered phase is more pervasive than previously suggested by experiment. [S0163-1829(98)01720-2]

I. INTRODUCTION

The bonding of aluminum with the transition metals is of scientific and technological concern. Despite this interest, the properties of ternary aluminides have received relatively little theoretical attention. In this paper, estimates of the phase stability of a major class of ordered ternary aluminides will be investigated by comparing the calculated heats of formation ΔH of the compounds and of the competing binary phases. The occurrence of ordered ternaries may be inferred from inspection of the binary transition-metal alloys: strong line compound formation usually arises when the transition metals are from the opposite ends of the row and, in addition, differences in atomic size encourage the elemental constituents to reside on their respective sublattices. The same is true for the transition metals when aluminum becomes the third alloy constituent. Roughly half the ordered ternary aluminides form in the antiphase Heusler BiF_3 structure with a M_2NAl composition. This structure is a bcc lattice with the M transition metals on the cube corners and the N and Al atoms alternately filling the body center positions in the x, y, and z directions. The observed occurrence[1] of these phases is indicated in Table I. Only one binary, Fe_3Al, is seen, but both from a symmetry point of view and the fact that the two Fe sites have markedly different magnetic moments, it is arguably a ternary. The gaps seen in the pattern suggest that a significant number of such phases remain to be observed. In this paper, we consider the cases of $M=$Au, Ni, Pd, Rh, Fe, and Ru and $N=$Y, Ti, Zr, V, Nb, and Mo (for $M=$Fe, $N=$Fe, Ni are considered as well). Except for Au, $3d$ and $4d$ elements were chosen with an eye towards dealing with a number of the known cases on the one hand, while filling in some of the blanks on the other. All but one of these 38 phases is stable relative to a three phase mixture of the elemental metals. The test for their occurrence thus involves competition with mixtures of elemental, binary, and higher order phases, thereby requiring estimates of ΔH for diverse competing phases. Of the systems that have been reported, the present estimates indicate that all but one occur. Of the unreported systems, some nine are predicted to exist while the other eighteen should be unstable. The advantage of having the calculations, of course, is having the ability to discern which of the unreported phases should not occur, as opposed to those that are yet to be observed.

The reported phases appearing in Table I suggest a pattern of occurrence and this view is supported by consideration of compounds where Ga and In replace Al. The observed compounds of Ga, whose size is similar to Al, lie in the same squares of the table as do those of Al. However, In, which is measurably larger, has compounds limited to the Sc and Ti blocks of the N elements. Comparison of the elemental volumes indicates that the compounds occur when the N atom and metalloid have volumes that are within 30–40% of one another. As will be clear from the results of this paper, volume is not the sole factor controlling the appearance of these phases since, as will be seen later, the individual columns of the table are not all ''yes'' or all ''no'' to such phase occurrences.

In this paper, we will concentrate on the competition of the BiF_3 structures with two and three phase mixtures of binary and elemental phases. In general, the composition of a ternary alloy can be represented by a triangle similar to Fig. 1: An alloy on a line connecting two binaries $A_{1-x}B_x$ ($\alpha=0$) and $B_{1-y}C_y$ ($\alpha=1$) has a composition $A_{(1-\alpha)(1-x)}B_{(1-\alpha)x+\alpha(1-y)}C_{\alpha y}$. The heat of formation for such a two-phase mixture is given by

$$\Delta H(\alpha)=(1-\alpha)\Delta H(A_{1-x}B_x)+\alpha\Delta H(B_{1-y}C_y).$$

For a ternary alloy to be stable relative to the two-phase mixture at the same composition, it must have a heat of formation more binding than $\Delta H(\alpha)$. In Fig. 1, the position of the ternary M_2NAl and some principal lines connecting competing binaries are shown. The relative lengths of these lines are simply related to α and, hence, to the heats of formation for the two-phase mixture. Similarly, the requirement for a possible three-phase mixture to occur with the correct stoichiometry is that the ternary phase be contained inside the triangle formed by connecting the three binary phases. (Note that two-phase mixtures are simply special cases of a three-phase mixture where the ternary lies on an edge of the triangle connecting the binary phases.)

TABLE I. The observed occurrence (cf. Ref. 1) of the M_2NAl compounds in the BiF_3 structure.

M \ N	Sc	Y	La	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W	Mn	Fe	Ni
Cu	●			●	●	●				●			●		
Ag	●														
Au	●			●		●							●		
Ni	●			●	●	●	●	●	●	●			●		
Pd	●				●	●							●		
Pt													●		
Co				●	●	●	●	●	●	●			●	●	
Rh													●		
Ir													●		
Fe				●			●			●	●		●	●	●
Ru															
Os															
Mn							●								

As an example, ΔH for the ternary Fe_2NbAl is compared to the various two-phase mixtures and the lowest calculated three phase mixture in Fig. 2. The phases shown provide a fair representation of those binaries that occur in the Fe-Nb, Fe-Al, and Nb-Al systems. The heat of the ternary is below all the lines (corresponding to those in Fig. 1), and thus the ternary would be expected to be stable relative to two-phase mixtures. Although the lowest calculated three-phase mixture is below these lines, it is still less binding than the ternary heat. Even though this system is a rather trivial case since ΔH for Fe_2NbAl is more binding than those any of the competing binary phases, it does demonstrate the competition between the ordered ternary and the binary phases. Of course, a ''no'' result where a pair (or multiple) of competing phases is more bound than the ternary is more conclusive than the ''yes'' seen here, but such comparisons are still useful in predicting whether some particular ordered BiF_3 ternary should be observable.

II. CALCULATIONS

In order to investigate the stability of the M_2NAl ordered ternaries, a large number of calculations for systems in a variety of crystal structures are required. Besides the compounds in the BiF_3 structure, the heats of both the elemental and the binary phases with which the ternary BiF_3 phases must successfully compete are needed. The intent is to calculate ΔH for the various compounds to a precision of about 0.01 eV/atom, given the choice of computational technique and (exchange-correlation) potential construct.

The calculations employ the full-potential linearized augmented Slater-type orbital method[2] (FLASTO) in which Slater-type orbitals are used to construct wave functions in the interstitial region, augmented by explicit solutions of the radial wave equations within nonoverlapping atomic spheres at each atomic site for orbital momenta up to $\ell = 8$. ''Full potentials'' are used, i.e., aspherical electron density and potential terms are kept throughout space. The core electrons

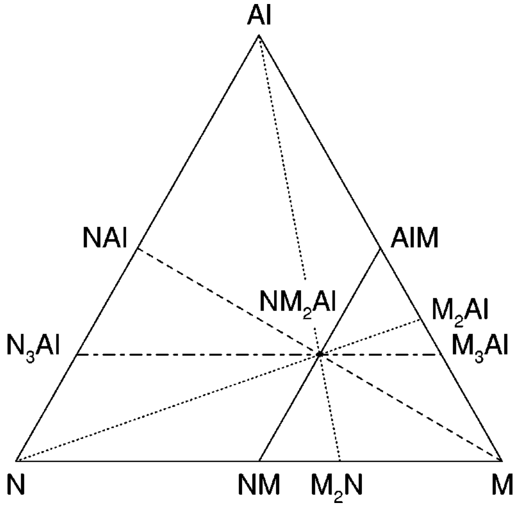

FIG. 1. The triangle for the phase diagram of the ternary N-M-Al system with the M_2NAl phase indicated. The lines, passing through this phase, connect pairs of binary phases which may compete as two-phase mixtures.

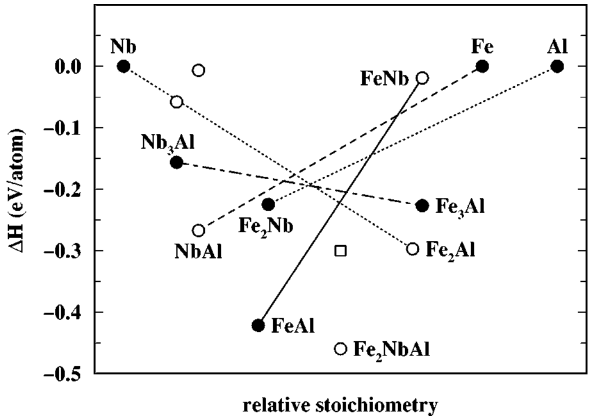

FIG. 2. The calculated heats of formation ΔH for Fe_2NbAl in the BiF_3 structure and competing binary and elemental phases. The filled (open) circles indicate observed (unobserved or hypothetical) phases. The segment lengths and relative positions of the lines (solid, dashed, etc.) connecting different phases correspond to those indicated in Fig. 1, all relative to the NM_2Al alloy. The heat for the most bound three-phase mixture is indicated by an open square.

are treated self-consistently and fully relativistically. Spin-orbit effects are neglected in the self-consistent treatment of the valence levels, but are included in a final iteration in most cases. When dealing with systems involving transition metals, FLASTO may be considered superior to any computational scheme neglecting aspherical terms and equal to or superior to any other scheme employed to estimate differences in energies between systems with the exception of the full-potential linearized augmented plane wave method[3] (FLAPW), which utilizes a more complete basis set in the interstitial region. The Hedin-Lundqvist form[4] for the local-density exchange and correlation potential is adopted.

Sets of special k points were increased in size until details such as the behavior of the energy in the vicinity of an extremum were accurately established. For the BiF_3 structure, calculations employing 110 and 182 k points in the irreducible wedge yielded energies in agreement with each other.

Slater-type orbital basis sets of varying size were employed with the largest involving 2 s-, 2 p-, 3 d-, 1 f-, and 1 g-like orbitals for the transition metals and 2 s-, 2 p-, a d-, and an f-like set for Al. When the LASTO scheme was originally developed, it was envisaged employing a single s, single p, and single d basis set, resulting in small matrices to construct and diagonalize and wave functions amenable to orbital population analyses. Such limited basis sets yield values of ΔH of inadequate accuracy; for example, if these small sets are employed to determine the optimum volume via minimization of the total energy, the lattice constants sometimes differ measurably from those obtained with more complete basis sets. The adverse experience here may have lessons for other computational schemes when they also employ single ζ-like basis sets. In order to minimize the systematic errors in the determination of ΔH for a compound, the total energies of the reference elemental metals were calculated with the same basis sets.

The crystalline lattices of the systems in question have been determined by energy optimization. Although some of the binaries form in the simple fcc- or bcc-like structures, many have more complicated structures involving both c/a (and b/a) ratios and internal atomic positions whose values are not determined by symmetry. The BiF_3 structure, on the other hand, is cubic with no such internal coordinates and only the crystal volume needs to be determined variationally. It is well established that LDA-based calculations yield lattice volumes that are smaller than those observed experimentally; for the systems at hand this difference is of numerical significance to the calculated ΔH. The lattice contractions are more important for the 3d elements and compounds than for the 4d and 5d counterparts. Our general experience when dealing with full potentials is that the calculated c/a ratios of the hexagonal and tetragonal structures (and b/a for the orthorhombic systems) are close to the observed values, and that the differences between the experimental and calculated values of these ratios have only a modest consequence on the energy to the accuracy aspired to here. Nevertheless, since the c/a (and b/a) ratios are of energetic significance and must be determined for the systems for which there is no crystallographic data, all the ΔH results used here were obtained from systems whose structure was optimized.

For those atomic positions not dictated by symmetry, optimizing them is often important on the scale of several hundredths of an eV/atom. It is more difficult to compare theory and experiment for internal atomic coordinates because much of the older crystallographic work determined these coordinates inaccurately or not at all. There is, however, the suggestion that modern crystallographic results and LDA-based predictions are, like the c/a ratios, in reasonable accord; the optimized and observed internal coordinates then yield essentially identical calculated energies.

III. RESULTS

The ΔH for ternary BiF_3 structures are listed in Table II. Except for Au_2MoAl, all are negative, implying that they are stable relative to a three-phase mix of the elemental solids. The heats of the competing binary phases will be reported elsewhere[5] as they require considerable discussion on their own.

As discussed above, Fe_2NbAl (Fig. 2) is calculated to be stable relative to the various two- and three-phase mixtures of the competing binary compounds. A different situation is shown in Fig. 3 for Pd_2VAl. While the pattern of the lines connecting the binary phases is much the same as for Fe_2NbAl, the ternary heat lies above two of the lines and is thus predicted to be unstable. As can be seen from the figure, the main reason that the ternary is unstable is the large heats of the Pd-Al binaries compared to either the V-Al or Pd-V ones. One line involves a pair of phases, Pd_3Al and V_3Al, which are not expected to occur. (Although V_3Al has been reported in the Cr_3Si structure, we find that the binary is unstable to other competing binary phases, in agreement with the generally accepted view of the V-Al binary phase diagram.) The fact the Pd_2VAl has lost out to a pair of phases that (probably) do not occur is as conclusive an indication that the ternary does not exist as is the loss to the observed pair.

As a final example, the competition for Fe_2ZrAl is shown in Fig. 4. Like Fe_2NbAl, both binary transition-metal aluminides have comparable heats, but as in the case of Pd_2VAl, some of these binary heats are larger than the ternary heat. (Both[6] $ZrAl_2$ and Zr_2Al_3 have $|\Delta H| > 0.5$ eV/atom and are not shown in the figure.) If only two-phase mixtures were considered, Fe_2ZrAl would be predicted to be stable. However, there are several three-phase mixtures that have greater binding than the ternary, with the largest heat for the $FeAl$-Fe_2Zr-$ZrAl_2$ mixture, thus suppressing the formation of the ordered BiF_3 phase.

Given the results of the figures, Fe_2NbAl is expected to occur while Pd_2VAl and Fe_2ZrAl are not. Similar comparisons, including a systematic comparison of all possible three-phase mixtures given the various binaries, have been done for the other 35 ternaries of Table II. The conclusions to be drawn from such comparisons are indicated in Table III. The question marks indicate cases that are close calls, i.e., the ternary is stable (or unstable) by an energy not much larger than the precision to which the ΔH were calculated. A pattern begins to appear in the table, namely, that the stable ternary phases are largely associated with having the N atom from the Ti column of the periodic table and the M from the Fe column. The tendency for Rh and Pd, and we expect Ir and Pt, to not form phases outside of the Ti group is likely

TABLE II. Calculated heats of formation ΔH and lattice constants a for compounds in the BiF_3 structure. The * indicate reported compounds.

Compound	ΔH (eV/atom)	a (a_B)
Au_2YAl	−0.74	12.699
Au_2TiAl*	−0.53	11.993
Au_2ZrAl	−0.58	12.408
Au_2VAl	−0.11	11.829
Au_2NbAl	−0.14	12.174
Au_2MoAl	+0.15	12.009
Ni_2YAl	−0.46	11.618
Ni_2TiAl*	−0.64	10.906
	−0.76, −0.78[a]	
	−0.58[b]	
Ni_2ZrAl*	−0.59	11.408
Ni_2VAl*	−0.41	10.729[c]
Ni_2NbAl*	−0.45	11.158
Ni_2MoAl	−0.20	10.988
Pd_2YAl	−0.85	12.258
Pd_2TiAl	−0.76	11.616
Pd_2ZrAl*	−0.80	12.041
Pd_2VAl	−0.44	11.454
Pd_2NbAl	−0.54	11.826
Pd_2MoAl	−0.17	11.672
Rh_2YAl	−0.82	11.995
Rh_2TiAl	−1.01	11.404
Rh_2ZrAl	−0.91	11.818
Rh_2VAl	−0.61	11.257
Rh_2NbAl	−0.61	11.651
Rh_2MoAl	−0.28	11.512
Fe_2YAl	−0.01	11.258
Fe_2TiAl*	−0.54	10.799
Fe_2ZrAl	−0.35	11.273
Fe_2VAl*	−0.53	10.571
Fe_2NbAl	−0.46	11.033
Fe_2MoAl*	−0.25	10.885
$NiFe_2Al$*	−0.11[d]	10.590
Fe_3Al*	−0.23[e]	10.586
	−0.32 ± 0.09[f]	
Ru_2YAl	−0.34	11.853
Ru_2TiAl	−0.75	11.358
Ru_2ZrAl	−0.63	11.753
Ru_2VAl	−0.62	11.205
Ru_2NbAl	−0.63	11.575
Ru_2MoAl	−0.29	11.435

[a] Calculations, Ref. 15.

[b] Calorimetry, Ref. 16.

[c] Reported a is apparently too large.

[d] Nonmagnetic compound less bound by 0.003 eV/atom; $\mu_{Fe} = 1.81$, $\mu_{Ni} = 0.64\mu_B$.

[e] Nonmagnetic compound less bound by 0.13 eV/atom; the majority (minority) Fe site moments are 1.56 (2.18) μ_B.

[f] Calorimetry, Ref. 9.

associated with the fact that the binary aluminides of these four elements have substantially[7] larger heats than do the other transition metal elements; it is competition from these binaries that suppresses the ternaries. In addition to the nine as yet unobserved phases that are predicted to occur, there is the suggestion that if consideration were extended to the 5d elements, on the order of twenty stable phases might be found.

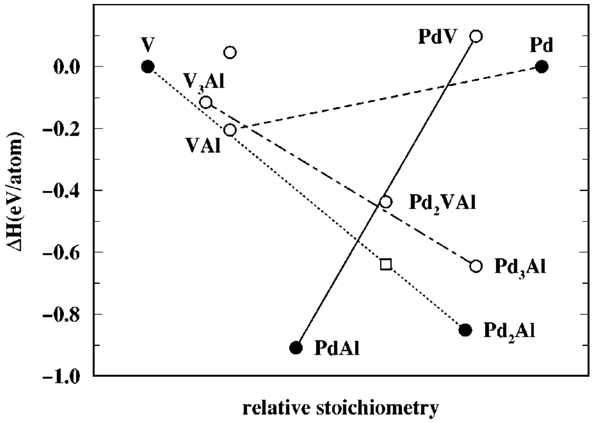

FIG. 3. The heats for Pd_2VAl in the BiF_3 structure and competing phases. See Fig. 2 for notation.

Of the phases that have been observed, all but one, Fe_2NiAl, is predicted to be stable. This discrepancy is troubling since the ordered ternary is predicted to have a significantly lower heat of formation than a large number of two- and three-phase mixtures. While magnetic effects could be important, the calculated Fe and Ni moments are not far from the elemental moments and so this is unlikely to be the explanation. (If there were a systematic error in the magnetic energy resulting from the local density approximation, this error would be expected to be larger for those systems whose magnetic moments differ most between the alloy and the elemental metals.) The calculated heats of the binary Ni-Al compounds are already large enough to suppress the ternary, but since these are in good agreement[8] with experiment, a reference energy problem is also unlikely. (Likewise, the Fe-Al heats, which are also in reasonable agreement with experiment,[7,9,10] would suppress the ternary.) Perhaps more puzzling is the fact that the calculated structural *and* magnetic properties of Fe_2NiAl are in excellent agreement with the experimental[11] values: the ratio of the volume[12] of the compound to the sum of the volumes of the elemental metals

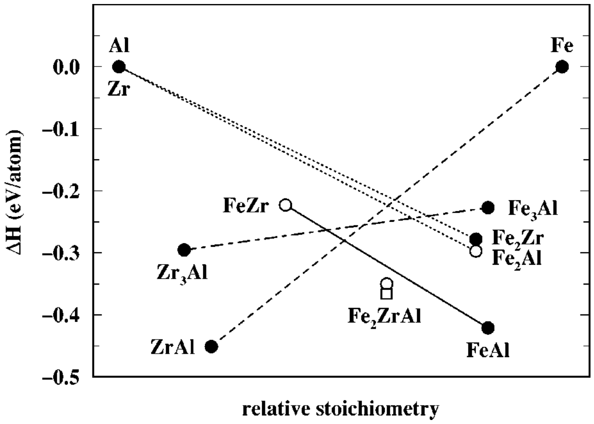

FIG. 4. The heats for Fe_2ZrAl in the BiF_3 structure and competing phases. See Fig. 2 for notation.

TABLE III. The observed (●) and calculated (Y: predicted to exist; N: predicted not to exist) occurrences of the M_2NAl compounds in the BiF_3 structure. The question marks indicate cases that are close calls.

M \ N	Sc	Y	La	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W	Mn	Fe	Ni
Cu	●			●	●	●				●			●		
Ag	●														
Au	●	Y?		●Y?	N?	●	N	N			N				
Ni	●	N		●Y	●Y?	●	●Y?	●Y	●	●	N		●		
Pd	●	N?		Y	●Y	●	N	N			N		●		
Pt													●		
Co				●	●	●	●	●	●	●			●	●	
Rh		N		Y	Y?		N	N			N		●		
Ir													●		
Fe		N		●Y	N?		●Y	Y		●	●Y?		●	●Y	●N
Ru		N		Y	Y?		Y	Y			N				
Os															
Mn							●								

experimentally is 0.934, while the calculated value is 0.935, and the experimentally determined low-temperature magnetic moment is $4.25\mu_B$ per formula unit, compared to the calculated value of $4.26\mu_B$.

While it is possible that the calculations are simply unable to reproduce the binding of this system, this explanation seems unlikely when the *whole* set of calculations is considered and the fact that other compounds with these elements yield ΔH values in reasonable agreement with experiment. Moreover, because Fe-Ni alloys have small heats, it is unlikely that the ternary would have a heat significantly larger than that calculated here. Another possibility is that the experimentally observed phase is metastable. Since this region of the Fe-Ni-Al phase diagram is a bcc field, one expects a bcc-based structure; whether it is ordered, disordered, or has short-range order is not possible for us to determine at present. From the experimental side, distinguishing[13] between BiF_3 or CsCl phases also may be hard, especially in the presence of short-range order. Further investigations, especially experimental, are needed to resolve this question.

Finally, we note that there is one experimental work[11] that has reported systems that did not form in the BiF_3, the same work that reported the existence of Fe_2NiAl. Of the systems considered in this work, attempts at forming both Fe_2ZrAl and Fe_2NbAl failed. As seen in Fig. 4, there is agreement that Fe_2ZrAl should not form, but for Fe_2NbAl (Fig. 2) there is again a disagreement. Again, the uncertainities in the calculated magnetic energies are too small to alter the theoretical prediction. For Fe_2NbAl to be unstable relative to two- or three-phase mixtures, at least one of the binary alloys must have a ΔH more binding than that of the ordered BiF_3 phase. For the Fe-Nb compounds, the calculated heat for Fe_2Nb is in good agreement with emf measurements[14] and this value places limits on the heats of the other observed Fe-Nb compounds; the net effect is that no Fe-Nb (Fe-Al, Nb-Al) alloy is expected to have a ΔH more binding than that of Fe_2NbAl. Thus, if Fe_2NbAl in the BiF_3 structure cannot be synthesized experimentally, it will most likely be either a disordered CsCl phase or a different ordered compound; the experimental work[11] does not comment on whether the samples were multiphase, disordered, etc.

IV. CONCLUSION

In this paper we have endeavored to calculate ΔH for a variety of ternary aluminides in the BiF_3 structure and for the competing binary phases. A number of these ternaries, which are as yet unreported, are predicted to exist. Inspection of Table III suggests that if the $5d$ transition-metal systems were considered as well, the number of phases that occur might almost double. The large number of such phases is not particularly surprising because all but Cu, Ag, and Mn of the M elements of Table III form aluminides having the CsCl structure. There are also significant numbers of CsCl structures formed between N and M elements, particularly when $N=$Sc or Ti and $M=$Ru. With the NM and MAl phases frequently lying on bcc lattices, it is not unexpected that at an intermediate composition an ordered ternary might also exist. However, the presence of such binaries does not guarantee the appearance of a ternary; e.g., RhAl and RhY both form in the CsCl structure, but the bonding of RhAl is so great that the ternary Rh_2YAl loses out in competition to the two-phase mixture. As discussed above, atomic volume also appears to be important in determining the occurrence of the BiF_3 structure; i.e., phase formation is discouraged if Al and the N atom are too different in size. Regardless, many ternary transition-metal aluminides are known to form in this phase and the present results indicate that more than half again as many remain to be observed.

ACKNOWLEDGMENTS

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