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Magnetic and Crystallographic Characteristics of the Ternary Intermetallic Compounds Containing Lanthanides and Iron or Cobalt†

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The ternary alloy systems $GdCo_{5-x}Al_x$, $GdCo_{5-x}Cu_x$ and $Ln_{1-x}Zr_xFe_2$ (with Ln = Gd, Dy, and Ho) have been studied to ascertain whether the antiferromagnetic coupling between the sublattices in the parent compound, $GdCo_5$ or $LnFe_2$, can be reversed by forming the ternary intermetallics. It was expected that replacement of Co with Al or Cu and of Ln with Zr would increase the electron concentration and in consequence the sign of the intrasublattice magnetic interactions might be reversed. Results showed the Gd–Co coupling remains antiferromagnetic up to the phase boundary, $x = 1.75$ and 4.20 for the Al- and Cu-containing ternaries, respectively. The saturation magnetization of ternaries indicates a steadily declining Co moment as Cu or Al is introduced. From the observed moments it is clear that cobalt absorbs electrons into its *d*-shell and at such a rate that the electron concentration is not increased by introducing Cu or Al.

Similar results were obtained for the $LnFe_2$-based ternaries and again it appears that the *d*-transition element, Fe, absorbs electrons at a rate to preserve a constant electron concentration. In both the Haucke and Laves phase systems it appears that Brillouin Zone filling is an important consideration. In both $GdCo_5$ and the $LnFe_2$ compounds the Fermi sphere seems to be in contact with a zone boundary so that increasing the electron concentration is energetically difficult and additional electrons are accommodated instead in essentially localized *d*-states associated with Fe or Co. This analysis provides a basis for understanding the phase boundaries in the $GdCo_5$-based systems and the nonexistence of $GdCu_5$, $GdAl_5$, and $ZrNi_2$.

The lattice parameters vary linearly with composition for all systems studied. $ZrFe_2$ is miscible in all proportions with $DyFe_2$ and $HoFe_2$, the ternaries all having the C 15 structure. $ZrFe_2$ and $GdFe_2$ have limited miscibility. The C 15 structure exists in $Gd_{1-x}Zr_xFe_2$ for $x = 0$ and for $x = 0.8$ to 1.0; the system consists of two phases for $0 \leqslant x \leqslant 0.8$.

I. Introduction

Intermetallics represented by the formula $LnCo_5$ and $LnFe_2$ (where Ln = Y or a lanthanide) have been receiving attention for a number of years (*1–10*). Interest in the cobalt containing intermetallics and in the copper-containing ternaries based on $LnCo_5$ has recently been heightened by the discovery (*11*) that some of these ternary systems are of significance commercially as permanent magnet materials. To date commercial interest has been limited to $LnCo_5$ systems containing light lanthanides; the Ln–Co magnetic coupling is antiferromagnetic for ternaries containing heavy lanthanides so that, in contrast with the situation for the light lanthanide counterparts in which the coupling is ferromagnetic, their intrinsic magnetization is small.

The Ln–Ln coupling in the elemental lanthanides and in intermetallics in which the second component is nonmagnetic is generally believed to result from the oscillatory polarization of the conduction electrons, the so-called RKKY interaction. The sign of this interaction is electron concentration dependent and there are instances (*12*, *13*) in which changes from antiferromagnetic to ferromagnetic coupling have been induced by deliberate alteration of the electron concentration. The nature of the Ln–Co interaction in the $LnCo_5$ and the Ln–Fe interaction in $LnFe_2$ compounds has not been clarified. If it is the RKKY interaction, then it should also be dependent on electron concentration and reversal might be induced by change in the electron concentration. Investigation of this point

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was the objective of the present study: to ascertain whether the antiferromagnetic Gd–Co coupling in $GdCo_5$ and the Ln–Fe coupling in $LnFe_2$ compounds can be reversed by introducing a third metallic component chosen so as to (hopefully) produce a rise in electron concentration. The practical importance of such a development is obvious. The issue is also of fundamental interest in that the results obtained may be helpful in elucidating the nature of interaction between the moments of the Ln and the *d*-transition metals in Laves or Haucke phase compounds. The systems studied were (a) $GdCo_{5-x}M_x$ with M = Cu or Al and (b) $Ln_{1-x}Zr_xFe_x$ with Ln = Gd Dy and Ho.

II. Experimental Details

Samples were prepared by levitation melting using the best grade metals available commercially—99.9% pure-grade Gd, Dy, and Ho and 99.999% or better Zr, Co, Cu, and Al. The Haucke phase samples ($GdCo_5$-based compounds) were used as cast without any heat treatment since preliminary work showed no improvement in sample quality by annealing, as judged from the diffraction pattern. The Laves phase samples were annealed for two or three weeks at temperatures ranging from 900°C for $ZrFe_2$ to 600°C for $LnFe_2$. Ternaries were annealed at intermediate temperatures in proportion to their $ZrFe_2$ content. Lattice parameters were obtained using a GE XRD-5 diffractometer, calibrated against NaCl. Magnetic measurements were made using equipment and techniques that are standard in this Laboratory and which have been described previously (*14*).

III. Experimental Results and Discussion

A. The $GdCo_5$-Based Haucke Phases

Results are largely summarized in Table I and in Figs. 1–3. The phase boundaries in the $GdCo_{5-x}Cu_x$ and $GdCo_{5-x}Al_x$ systems occur at $x = 4.20$ and 1.75, respectively. Throughout the range of the terminal phases the lattice parameters vary linearly with x within the precision of the measurements, ±0.01 A. Representative magnetization-temperature results are shown in Figs. 1 and 2. These results, together with the saturation moments shown in Fig. 3, indicate that the antiferromagnetic Gd–Co coupling in $GdCo_5$ persists in the two ternary systems studied.

Neutron diffraction measurements on various $LnCo_5$ compounds indicate (*15*, *16*) a cobalt moment ranging from 1.50 to 1.72 μB, the higher moment occurring in compounds with highest spin for the Ln component. Although $GdCo_5$ has not been investigated (because of the high neutron capture cross section of Gd), it is reasonable to suppose that the cobalt moment in $GdCo_5$ lies in the range 1.64 μB, the value found (*15*) in $TbCo_5$, to 1.72 μB, the moment found in $HoCo_5$ (*16*) and in elemental cobalt. Taking the moment of Gd in $GdCo_5$ to be 7.00 μB, the cobalt moment in this compound can be computed from the observed $GdCo_5$ saturation moment—1.55 μB per formula

TABLE I

SUMMARY OF STRUCTURAL AND MAGNETIC INFORMATION

	$GdCo_{5-x}Cu_x$				$GdCo_{5-x}Al_x$			
x	a_0(A)	c_0(A)	μ_{sat}[a]	μ_{Co}[b]	a_0(A)	c_0(A)	μ_{sat}[a]	μ_{Co}[b]
0	4.98	3.98	1.55	1.71	4.98	3.98	1.55	1.71
0.25					5.00	3.99	1.10	1.71
0.50	4.99	3.99	0.65	1.70				
1.00	4.98	4.00	0.46	1.64	5.01	4.04	2.16	1.21
1.50					5.04	4.06	3.99	0.86
1.75					5.05	4.07	4.85	0.66
2.00	5.00	4.02	2.48	1.51				
3.00	5.01	4.04	4.40	1.30				
4.00	5.02	4.07	6.28	0.72				
4.20	5.03	4.08	6.43	0.71				

[a] Saturation magnetization at 4.2°K in μB per formula unit.

[b] Value of the cobalt moment in μB per atom calculated under the assumptions that the Gd moment is 7.00 μB and the Gd–Co coupling is antiferromagnetic.

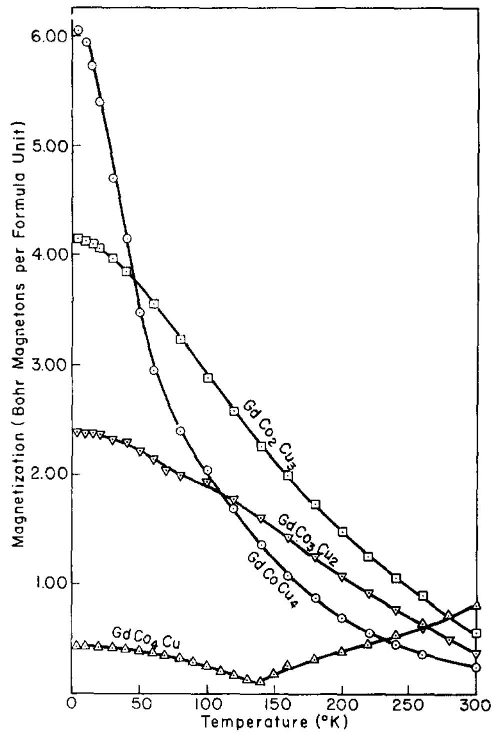

FIG. 1. Magnetization versus temperature for $GdCo_{5-x}Cu_x$ alloys measured in an applied field of 19 kOe.

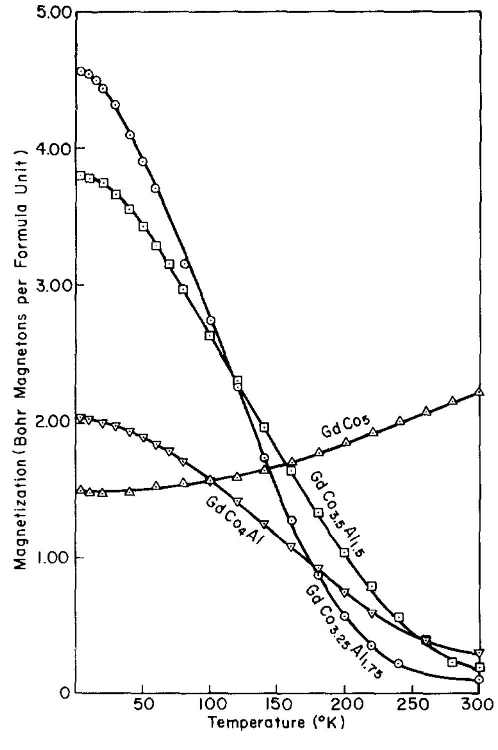

FIG. 2. Magnetization versus temperature for $GdCo_{5-x}Al_x$ alloys measured in an applied field of 19 kOe.

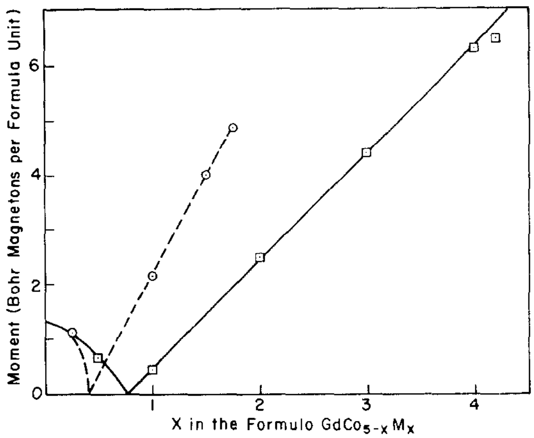

FIG. 3. Saturation moments at 4.2°K for $GdCo_{5-x}Cu_x$ (□) and $GdCo_{5-x}Al_x$ (o) alloys.

unit—to be 1.71 μB. If the Gd moment is regarded as constant at 7.00 μB for the ternaries in the present study, the moments of cobalt listed in columns 5 and 9 of Table I are obtained. A decrease in cobalt moment as Cu or Al is introduced into the cobalt sublattice is readily apparent.

Initially it seemed surprising that the Gd–Co coupling was unmodified by changing electron concentration. In other cases, e.g., in the Eu_xLa_{1-x}-Al_2 system (*12*), the coupling mode was reversed by changing electron concentration. The change in cobalt moment discussed in the preceding paragraph suggests why reversing in coupling does not occur in the $GdCo_5$-based ternaries. The decline in cobalt moment indicates electron absorption by cobalt when Al or Cu is introduced into $GdCo_5$; vacancies in the cobalt d band serve as traps for the extra electrons which are introduced so that the actual electron concentration is not increased as cobalt is replaced by Cu or Al. Results can be interpreted in terms of the conceptual framework suggested in earlier studies carried out in this Laboratory. In previous studies of similar ternaries it was clear that while the *d*-electrons in cobalt (or iron) in ternaries of the form $LnT_{2-x}Al_x$ (where T = Fe or Co) are neither fully localized or completely delocalized, they more nearly behave as localized electrons (*17–19*). (For example, they exhibit Curie–Weiss behavior.) One can reasonably postulate similar behavior, i.e., the *d*-electrons behaving as more nearly localized, for the closely related Haucke phase involved in the present study. If so, the observed cobalt moment can be employed to estimate the electrons contributed or absorbed by cobalt (*20*). In $GdCo_5$ this reasoning leads one to describe cobalt on the average as $3d^{8.3}$ and, hence, contributing 0.7 electrons per atom to the collection of delocalized electrons. In $GdCo_{3.25}Al_{1.75}$, by contrast, the cobalt moment indicates that it is on the average in a $3d^{9.3}$ configuration and, hence, has absorbed 0.3 electrons per atom. Thus, one obtains for the electron concentration (e.c.) the following:

for $GdCo_5$,

$$\text{e.c.} = \frac{1 \times 3 + 5 \times 0.7}{6} = 1.1;$$

for $GdCo_{3.25}Al_{1.75}$,

$$\text{e.c.} = \frac{1 \times 3 + 3.25 \times (-0.3) + 1.75 \times 3}{6} = 1.2;$$

and for $GdCo_{0.8}Cu_{4.2}$,

$$\text{e.c.} = \frac{1 \times 3 + 0.8 \times (-0.3) + 4.2 \times 1}{6} = 1.2.$$

Similar calculations for all the compositions shown in Table I give e.c. ranging from 1.0 to 1.2. It is thus clear that cobalt absorbs electrons at a rate to hold the e.c. essentially constant. Perhaps it is for this reason that replacement of cobalt with Cu or Al fails to convert antiferromagnetic $GdCo_5$ into a ferromagnetically coupled material.

The variations of magnetization with temperature shown in Figs. 1 and 2 are almost exclusively due to disordering within the Gd sublattice. Order on the cobalt sublattice breaks down at temperatures well above the range covered in the present study. The variation of moment with composition is, as noted above, consistent with ferrimagnetism in these materials. The positive deviations noted near the minimum in the curve in Fig. 3 are similar to those noted in earlier studies (*21*). Near the minimum the molecular field is weak and the applied field is strong enough to begin to convert the ferrimagnetic materials into a ferromagnetically aligned substance.

The Brillouin Zone structure for the $GdCo_5$ structure is instructive in respect to the behavior of the $GdCo_5$-based ternary alloys. The first, second and third zones are formed from the 100 and 001, the 101 and the 110, and the 002 planes, respectively. The electron concentration is such that the first and second zones are completely filled; the third, which has a capacity of 1.85 electrons/atom, is partly filled. The inscribed Fermi sphere contacting the 110 faces contains 0.99 electrons/atom; the inscribed sphere contacting the 002 faces contains 1.49 electrons/atom. These features suggest why $CaCu_5$ (e.c. = 1.17) and $GdCo_5$ (e.c. = 1.08) form whereas isostructural $GdCu_5$ (e.c. = 1.33) does not form. The sequence of events as Co in $GdCo_5$ is replaced by Cu or Al is probably as follows: Initially as Co is replaced, the rise in e.c. is prevented by electron absorption by cobalt. As the negative charge on cobalt develops, it becomes energetically difficult to add further electrons unless the Fermi energy is increased. Since the Fermi sphere is in contact with the zone boundaries (at the 110 faces), addition of electrons will produce a sharp rise in energy which destabilizes the phase. This curtails additional replacement of cobalt by copper or aluminum and it is apparently for this reason that $GdCu_5$ and $GdAl_5$ in the Haucke phase structure do not form.

B. The $LnFe_2$-based Laves Phase Systems

Results are largely summarized in Table II and in the diagrams given in Figs. 4–6.

The data shown in Figs. 5 and 6 make it clear that the antiferromagnetic Ln–Fe coupling in the $LnFe_2$ compounds is unchanged by partial replacement of Ln with Zr. The decline in moment as x is decreased from 1 to 0.7 (Fig. 6) is due to the antiferromagnetic nature of this alloy. From the measured saturation magnetization the Fe moments are estimated to be 1.7, 1.7, and 1.9 in $ZrFe_2$, $HoFe_2$, and $DyFe_2$, respectively. Assuming the free ion moment for Dy and Ho (10 μB), one expects compensation at $x = 0.68 \pm 0.02$. By extrapolation one finds experimentally zero moment at x equalling approximately 0.63, in keeping with the notion that these ternaries are ferrimagnetic.

The $ZrFe_2$–$GdFe_2$ is unusual in that no detectable Zr can be incorporated into the Gd sublattice in $GdFe_2$ and only 20% of Zr in $ZrFe_2$ can be replaced by Gd. This is in contrast with complete miscibility

TABLE II

SATURATION MAGNETIZATIONS OF THE TERNARY LAVES PHASES

	μ_{sat} (Bohr Magnetons/Formula Unit)		
x	$Ho_{1-x}Zr_xFe_2$	$Dy_{1-x}Zr_xFe_2$	$Gd_{1-x}ZrFe_2$
0	6.52	6.25	3.21
0.1	5.11		2.99
0.2	4.23	4.28	2.45
0.3	3.23		↑
0.4	2.34	2.27	
0.5	1.53		
0.6	0.91	0.99	two-phase
0.7	0.85		system
0.8	1.48	1.62	
0.9	2.37		↓
1.0	3.40	3.40	3.40

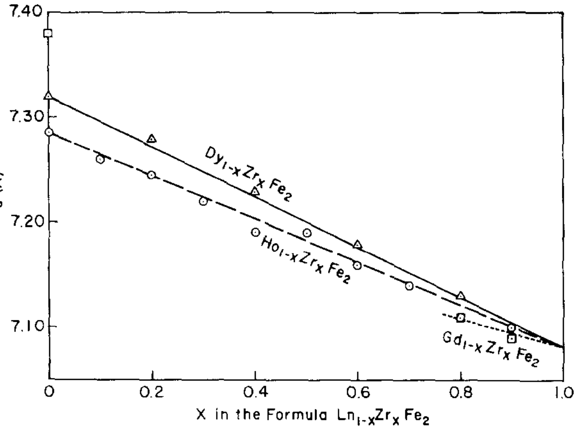

FIG. 4. Lattice parameters for $Ln_{1-x}Zr_xFe_2$ alloys.

in the $ZrFe_2$–$DyFe_2$ and $ZrFe_2$–$HoFe_2$ systems. The factors responsible for the different behavior of $GdFe_2$ are not understood. Because of the solubility limit the magnetic behavior in the Gd-containing ternaries cannot be investigated except between $x = 0.8$ and 1.0. Even though the accessible composition range is limited, the results clearly indicate ferrimagnetism in the $Gd_{1-x}Zr_xFe_2$ ternaries.

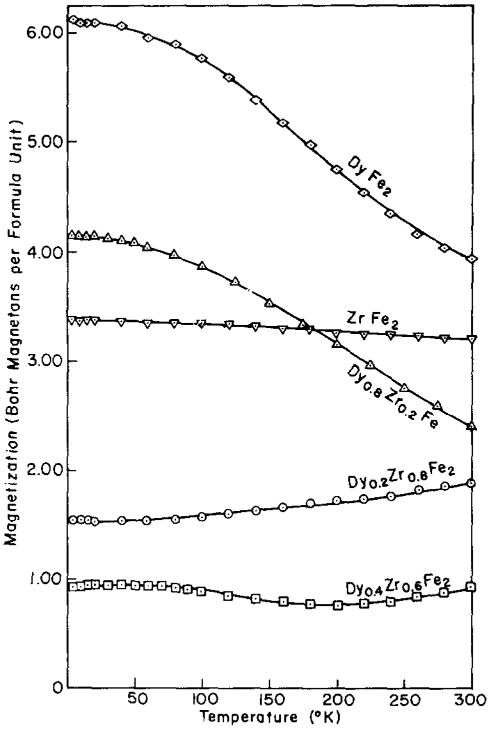

FIG. 5. Magnetization-temperature data for $Dy_{1-x}Zr_xFe_2$ alloys. The magnetization was measured in an applied field of 19 kOe.

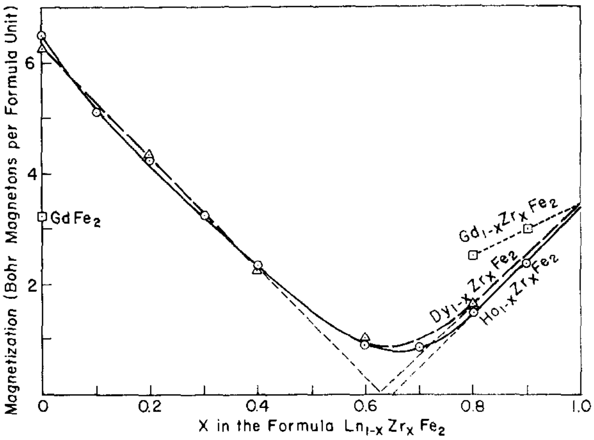

FIG. 6. Saturation moments at 4.2°K for $Ln_{1-x}Zr_xFe_2$ ternaries.

It appears that the failure to achieve an alteration in coupling by introducing a third component is brought about by an effect similar to that operating in the $GdCo_5$-based systems described above; as Zr is introduced, the Fe absorbs electrons at a rate to prevent a rise in e.c. The evidence in this case is, however, less direct. To appreciate the factors operating it is appropriate to consider the series $GdNi_2$, $GdCo_2$, and $GdFe_2$. The d-transition metal in this series has moments 0, 1.1, and 1.9 μB per atom (*8*, *9*). Using the same reasoning as employed in the consideration of the $GdCo_5$–based ternaries, it is concluded that the Ni and Co are in $3d^{10}$ and $3d^{8.9}$ configurations, respectively. It seems reasonable to suppose that Fe, being one electron poorer than Co, is in a $3d^{7.9}$ configuration. If so, its moment would suggest that its d-shell contains on the average 4.9 electrons with plus spin and 3.0 with a minus spin. The situation for Fe, Co, and Ni in the Gd compound and in $ZrFe_2$ is summarized in Table III. The results for $ZrFe_2$ are obtained under the assumption that one electron from Zr is absorbed by the two Fe atoms. This assumption accounts for the Fe moment in $ZrFe_2$ (1.7 μB) within 0.1 μB. In summary, the general trend in the Ni, Co, Fe sequence together with the differences in Fe moment between $ZrFe_2$ and $GdFe_2$ (and presumably likewise for $HoFe_2$ and $DyFe_2$) suggests that progressive replacement of Ln by Zr leaves the electron concentration unchanged.

Suggestive evidence in support of the rather speculative ideas set forth in the preceding paragraph is provided by the work of Oesterreicher and Wallace (*18*) on the $GdCo_{2-x}Al_x$ and $ErCo_{2-x}Al_x$ systems and by unpublished work in this Laboratory on $GdNi_{2-x}Cu_x$ system (*22*) and a large number of

TABLE III

d-ELECTRON CONFIGURATIONS AND ELECTRON CONCENTRATIONS

	n_+	n_-	Net Spin	Total *d*-Electrons	Fe, Co or Ni Contribution to e.c.	e.c.
$GdNi_2$	5	5	0	10	0	1.0
$GdCo_2$	5	3.9	1.1	8.9	0.1	1.1
$GdFe_2$	4.9	3.0	1.9	7.9	0.1	1.1
$ZrFe_2$	5.0	3.4	1.6	8.4	−0.4	1.1

systems (*23*) represented by the formula $LnNi_{2-x}Al_x$. In each case the C 15 structure for $LnNi_2$ or $LnCo_2$ became unstable and no longer could be formed for electron concentrations greater than about 1.15. This result has been interpreted in terms of Brillouin Zone filling effects. The e.c. postulated for $GdFe_2$ and $ZrFe_2$ is remarkably close to this value, so close that it appears that the Fe and Co configuration may be controlled by the Fermi Surface–Brillouin Zone interaction. These metals in $LnFe_2$ or $ZrFe_2$ release electrons to or absorb electrons from the conduction band so as to produce a Fermi surface which just contacts the zone boundary; hence, the e.c. is unchanged by varying the Ln-to-Zr ratio. Hypothetical $ZrNi_2$, which does not exist in the C 15 structure, would have an e.c. of 1.33. This is beyond the stability range found for the $LnNi_2$- and $LnCo_2$-based ternaries (*22*, *23*) referred to above. Viewed in this context the nonexistence of $ZrNi_2$ is understandable; otherwise, it is not since the relative sizes of Zr and Ni are appropriate.

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