Observation of a pair-breaking field in the magnetically diluted antiferromagnetic superconductor $DyNi_2B_2C$

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^{57}Fe Mössbauer studies of $Dy_{0.8}R'_{0.2}Ni_2B_2C$ (R'=Y, Lu) and $Dy_{0.92}La_{0.08}Ni_2B_2C$ doped with 1 at. % ^{57}Fe exhibit the appearance of a magnetic hyperfine field B_{hf} at the ^{57}Fe(Ni) site below the antiferromagnetic (AF) ordering temperature $T_N \sim 10$ K. Such a hyperfine field does not exist in pure AF $DyNi_2B_2C$. This hyperfine field can explain the reduction in the superconducting transition temperature for $Dy_{0.8}Y_{0.2}Ni_2B_2C$, however, it is too small to explain the complete breakdown of superconductivity in the case of La and Lu doping, respectively.

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I. INTRODUCTION

Coexistence of superconductivity and commensurate antiferromagnetic (AF) order is observed in the rare earth (R) nickel borocarbides RNi_2B_2C (R=Dy and Ho). The superconducting transition temperature T_c of $DyNi_2B_2C$ rapidly decreases if Dy is substituted by non-magnetic Lu ($T_c < 2$ K for a Lu concentration $x=0.15$) as has been found by Cho *et al.*[1] The authors of this paper claim that this is an indication of *complete breakdown of de Gennes scaling*, without giving a really satisfying explanation for the reduction of T_c. The work of Morozov,[2–4] however, in principle can explain this reduction: according to this work the effect of nonmagnetic impurities in antiferromagnetic superconductors in the region of coexistence of superconductivity and antiferromagnetism is analogous to the pair-breaking effect of paramagnetic impurities in ordinary superconductors. The reentrant behavior of $HoNi_2B_2C$ in the temperature region $5<T<6$ K, where this compound shows incommensurate magnetic order, can be explained in a similar way.[3,4]

We have shown in previous papers[5–7] that a pair-breaking field at the Ni site can be observed by ^{57}Fe Mössbauer spectroscopy for ^{57}Fe doped *non*-superconducting RNi_2B_2C (R=Tb, Gd) and for $HoNi_2B_2C$ in the reentrance region. Such a pair-breaking field at the Ni site seems to exist only for R magnetic moment configurations which differ from the commensurate AF order (the latter one shows *no* pair-breaking field). This fact can be explained in a rather simple way: the observed magnetic hyperfine (hf) field $\boldsymbol{B}_{hf}$ at the Ni site in RNi_2B_2C is a transferred or dipolar field only, i.e., it results from the magnetic moments $\boldsymbol{m}_j$ of the j neighboring R atoms: $B_{hf} \propto \Sigma_j \boldsymbol{m}_j$. This sum is zero for commensurate AF only. Therefore, one should expect that such a pair-breaking field also should be observable in magnetically diluted AF superconductors. It is for that reason that we have studied ^{57}Fe doped (1 at. %), magnetically diluted $DyNi_2B_2C$, i.e., $Dy_{0.8}R'_{0.2}Ni_2B_2C$ (R'=Y, Lu) and $Dy_{0.92}La_{0.08}Ni_2B_2C$, by ^{57}Fe Mössbauer spectroscopy.

II. SAMPLE PREPARATION AND CHARACTERIZATION

Polycrystalline samples of nominal formula $(Dy_{0.8}R'_{0.2})Ni_2B_2C$ (R'=Y, La, Lu) doped with 1 at % of ^{57}Fe where prepared by argon arc melting of stoichiometric amounts of high-purity elements and heat treated in the standard method.[8] Powder x-ray diffraction measurements at room temperature, using Cu $K\alpha$ radiation Rigaku diffractometer, and a subsequent Rietveld refinement analysis were made for structural characterization. Temperature dependent ^{57}Fe Mössbauer effect (ME) measurements were performed in transmission geometry using a variable temperature He cryostat. The ^{57}Co:Rh ME source always was kept at the same temperature as the sample.

III. EXPERIMENTAL RESULTS

Figure 1 shows as an example the x-ray diffraction pattern of the $Dy_{0.8}Lu_{0.2}Ni_2B_2C$ sample. The Rietveld analysis of the diffraction patterns for $(Dy_{0.8}R'_{0.2})Ni_2B_2C$ (R'=Y and Lu) compounds essentially shows nearly single phases, with good crystallinity, corresponding to the expected $LuNi_2B_2C$ type of structure. Very small extra peaks corresponding to an impurity phase (<5%) have been observed for some of the compounds.

On the other hand, considering the miscibility gap observed in other La diluted RNi_2B_2C systems (Refs. 9–11), the synthesization of $Dy_{1-x}La_xNi_2B_2C$ would be very difficult. Therefore, as expected, the presence of a minor second (La-rich) phase (~25%) of $LuNi_2B_2C$ type was observed in the $Dy_{1-x}La_xNi_2B_2C$ compound and included in the x-ray analysis to obtain a good refinement. In spite the mismatch between nominal and real concentration of La found for this

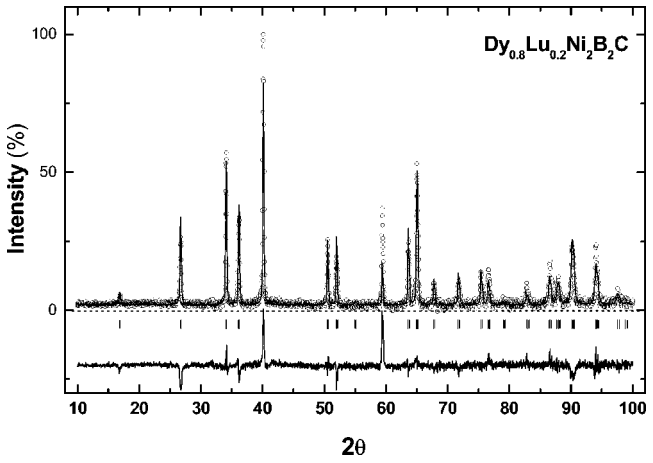

FIG. 1. Room temperature x-ray diffraction pattern of the $Dy_{0.8}Lu_{0.2}Ni_2B_2C$ sample. The structural and conventional Rietveld parameters are shown in Table I.

compound ($x=0.08$), it is still useful for our purpose and, as we will see forward, the results obtained from it will not alter the conclusions which are obtained in this work. Actually, we only need a $Dy_{1-x}La_xNi_2B_2C$ sample with a given La concentration small enough to prevent superconductivity. In fact, our sample fulfills that requirement since because the presence of just only 1% ($x=0.01$) of La is enough to completely destroy superconductivity.[9,12]

Mössbauer spectra at room temperature of the samples $Dy_{0.8}R'_{0.2}Ni_2B_2C$ ($R'=$Y, Lu) and $Dy_{0.92}La_{0.08}Ni_2B_2C$ are shown in Fig. 2. The spectra show as a main component a quadrupole doublet attributed to Fe at the Ni site in the RNi_2B_2C phase. An additionally small doublet (~15% of the absorption area) is also observed and attributed to an impurity phase (probably *R*NiBC for $R'=$Y, Lu and a minor $LuNi_2B_2C$ phase for $R'=$La). The linewidth of the La doped sample is slightly larger than that of the other samples probably due to the fact the large La atoms produce larger distortions of the lattice (see next section).

Low temperature Mössbauer spectra of the $Dy_{0.8}Lu_{0.2}Ni_2B_2C$ compound are shown in Fig. 3. As the temperature is lowered below 10 K a slight but perceptible broadening occurs. The fitting procedure and analysis of these spectra will be discussed in Sec. IV.

IV. DISCUSSION

Doping antiferromagnetically ordered $DyNi_2B_2C$ with a nonmagnetic R' atom essentially has four different effects: (i) change of (c'/a) parameter (c' is the distance of the two

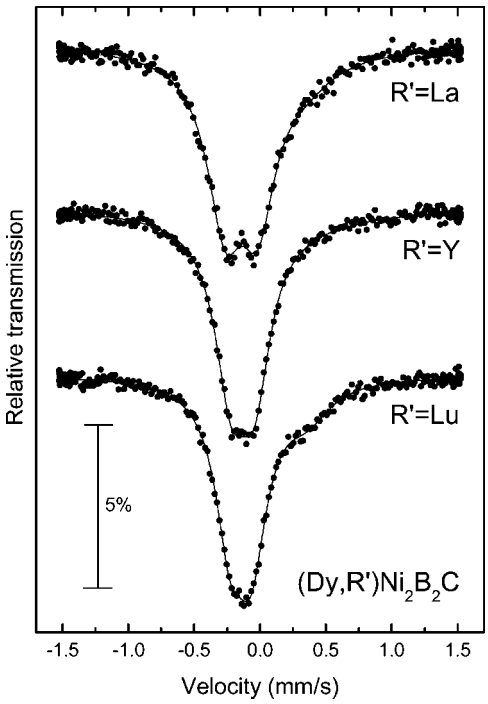

FIG. 2. Room temperature ^{57}Fe Mössbauer spectra of $Dy_{0.8}R'_{0.2}Ni_2B_2C$ ($R'=$Y, Lu) and $Dy_{0.92}La_{0.08}Ni_2B_2C$.

R-C layers between which the NiB_4 tetrahedra are sandwiched and a is the lattice parameter in the basal plane) which is a measure for the distortion of the NiB_4 tetrahedra, (ii) appearance of lattice distortions due to the fact that the R' and Dy atom have different atomic radii, (iii) creation of a pair-breaking field due to magnetic dilution, and (iv) pair-breaking effect of nonmagnetic impurities analogous to that of paramagnetic impurities in nonmagnetic superconductors.[2–4] All these effects will influence T_c in different ways: effect (i) will increase or decrease T_c depending whether the (c'/a) parameter is increasing or decreasing relative to that of $DyNi_2B_2C$; effect (ii) may reduce T_c in connection with effect (iv) since distortions in *non*-magnetic superconductors have only very small effects on T_c (Ref. 13); effects (iii) and (iv) always will lower T_c. Information on the structural effects (i) and (ii) are obtained from XRD x-ray diffraction data and ^{57}Fe ME spectra taken at $T>T_N$, while information on effect (iii) is obtained from ^{57}Fe ME spectra taken below T_N. In the following we first will discuss the information obtained on the structural effects (i) and (ii) and then go to the magnetic effects (iii) and (iv), especially the observation of a pair-breaking field.

TABLE I. La concentration, lattice parameters, and conventional Rietveld *Rp*, R_{wp}, R_{exp} (%) and goodness of fit as obtained from the analysis of room temperature x-ray diffractograms of $Dy_{1-x}R'_xNi_2B_2C$ ($R'=$Y, La, Lu).

R'	x	a	c	R_p	R_{wp}	R_{exp}	Goodness of fit
Y	0.2	3.530(2)	10.500(3)	2.47	4.22	3.08	1.87
La[a]	0.08	3.546(4)	10.449(4)	3.48	6.08	3.91	2.42
Lu	0.2	3.517(2)	10.521(3)	2.72	4.65	3.35	1.93

[a]The values of the parameters correspond to the main phase.

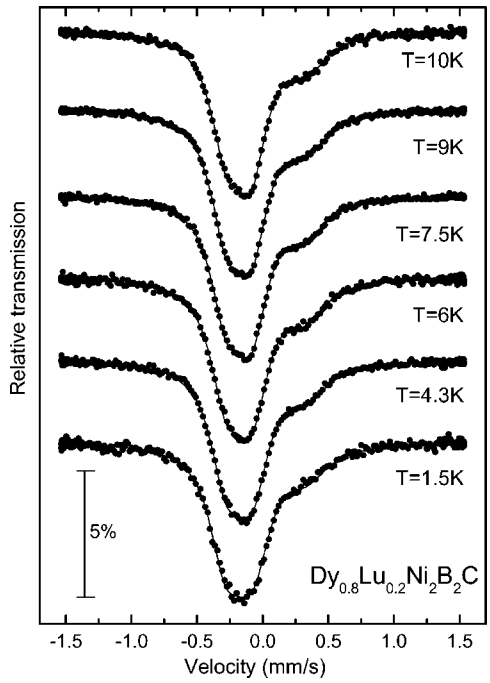

FIG. 3. ^{57}Fe Mössbauer spectra of $Dy_{0.8}Lu_{0.2}Ni_2B_2C$ for 1.5 K $\leqslant T \leqslant$ 10 K.

A. Structural effects

In former publications we have shown[14] that there exists a universal linear correlation between the (c'/a) parameter and the observed quadrupole splitting ΔE_Q for the $R\mathrm{Ni_2B_2C}$ as well as the RNiBC compounds. The (c'/a) parameters as calculated from the XRD data and the measured ΔE_Q values as obtained from the room temperature ^{57}Fe ME spectra (see Fig. 2) have been plotted in Fig. 4 for $Dy_{0.8}R'_{0.2}Ni_2B_2C$ (R'=Y, Lu) and $Dy_{0.92}La_{0.08}Ni_2B_2C$ together with the corresponding data of the pure $R\mathrm{Ni_2B_2C}$ compounds.[14] It is quite evident from Fig. 4 that the data points of the doped compounds $Dy_{0.8}R'_{0.2}Ni_2B_2C$ and $Dy_{0.92}La_{0.08}Ni_2B_2C$ fit well to this universal correlation between (c'/a) and ΔE_Q found for the pure compounds. Since the (c'/a)— as well as ΔE_Q—values for $Dy_{0.8}R'_{0.2}Ni_2B_2C$ and $Dy_{0.92}La_{0.08}Ni_2B_2C$ are averaged values [both (c'/a) and ΔE_Q will have local variations] it follows from the earlier finding that the ^{57}Fe atoms are homogeneously distributed in the doped compounds. The (c'/a) value for the La doped sample is larger and for the Lu doped sample is smaller than that of the compound. Just taking the correlation between (c'/a) and T_c found for the nonmagnetic or antiferromagnetically ordered $R\mathrm{Ni_2B_2C}$ compounds,[15] one could conclude that T_c should be decreased in the case of La doping and increased for Lu doping, providing that there are no other effects on T_c. However, since this is in clear contradiction to the experimental finding of a reduced T_c in both cases, one has to conclude that the other effects are dominant.

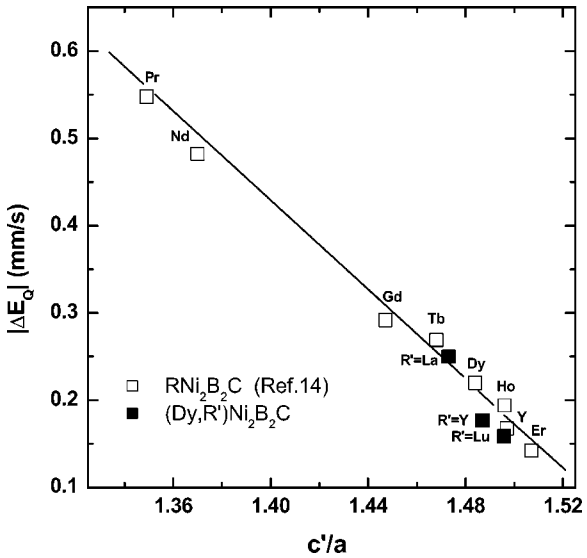

FIG. 4. Room temperature quadrupole splitting $|\Delta E_Q|$ as a function of c'/a parameter for $Dy_{0.8}R'_{0.2}Ni_2B_2C$ (R'=Y, Lu) and $Dy_{0.92}La_{0.08}Ni_2B_2C$. The corresponding data for the pure $R\mathrm{Ni_2B_2C}$ compounds also are plotted (from Ref. 14).

TABLE II. Differences $\Delta r = r(R') - r$ (Dy) of atomic radii and the observed ^{57}Fe ME linewidths at T=10 K for $Dy_{0.8}R'_{0.2}Ni_2B_2C$ (R'=Y, La, Lu).

R'	Y	La	Lu
Δr (nm)	0	+0.016	−0.006
Linewidth (mm/s)	0.25	0.34	0.27

The amount of local lattice distortions can be estimated from the observed linewidths of the ME quadrupole doublets. Variations in the local structure around ^{57}Fe will lead to a variation in ΔE_Q and thus to an increase in the ME line width. In Table II the differences Δr in the atomic radii together with the observed ^{57}Fe ME line widths at T=10 K are given for all doped compounds studied. La having the largest deviation in size with respect to Dy is causing a broader ME line width in $Dy_{0.92}La_{0.08}Ni_2B_2C$ compared to that found in $Dy_{0.8}Lu_{0.2}Ni_2B_2C$ or in $Dy_{0.8}Y_{0.2}Ni_2B_2C$ where Dy and Y have very similar size. The lattice distortions, therefore, are the largest for the La doped samples while they are almost negligible for Y doping. We will come back to this point when we discuss the magnetic effects on T_c.

Neutron diffraction studies[16] have shown a slight thermal contraction in $R\mathrm{Ni_2B_2C}$ compounds as temperature decreases: the lattice contracts down to ~50 K and for lower temperatures, where superconductivity appears, it remains almost constant.[16] The ΔE_Q values for all the samples studied here increase slightly with increasing temperature as expected from the point charge model for ΔE_Q. For the analysis of the low temperature Mossbauer spectra we fixed the ΔE_Q value to that found at 10 K and allowed the other parameters freely vary (see next chapter).

B. Magnetic effects

The ^{57}Fe ME spectra taken at temperatures below $T_N \approx 10$ K show some small deviations compared to those for $T > T_N$ (e.g., Fig. 3), indicating the presence of a small mag-

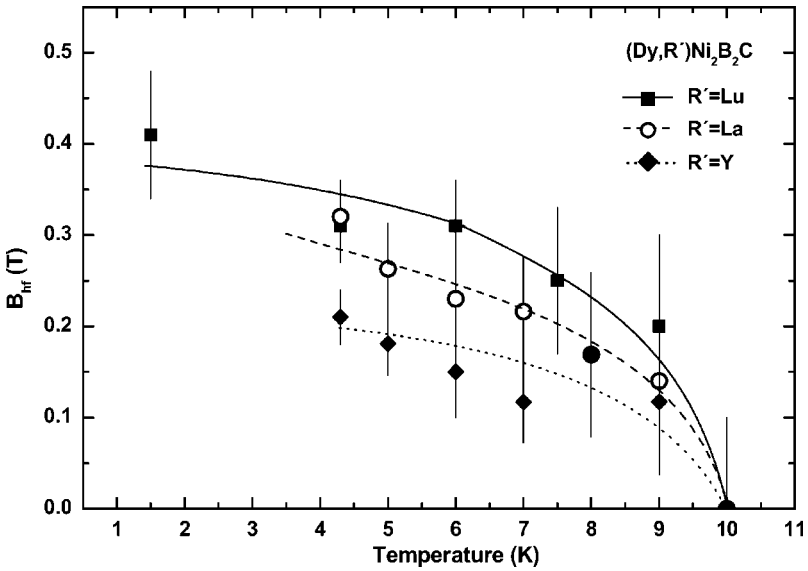

FIG. 5. Temperature dependence of transferred magnetic hyperfine field B_{hf} at ^{57}Fe for $Dy_{0.8}R'_{0.2}Ni_2B_2C$ ($R'=$Y, Lu) and $Dy_{0.92}La_{0.08}Ni_2B_2C$.

netic hyperfine field B_{hf}. In order to fit these spectra we had to make the following simplification: the spectra have been fitted with only one component, taking the full Hamiltonian with the ΔE_Q value as obtained for $T > T_N$, free values for B_{hf} and an angle $\theta = 55°$ (so called magic angle) between V_{zz} and B_{hf}. The latter takes into account that we will observe only an average of the angles between B_{hf} and V_{zz} for the different configurations of R' around Fe. In reality the measured ^{57}Fe ME spectra are the sum of different subspectra each of which differs in the number of R' and Dy nearest neighbor (nn) atoms. For $x = 0.2$ and a total number of 4 nn rare earth atoms (either R' or Dy) there is a probability of about 40% for having no R' nn atom, of about 40% for having one R' nn atom, and of about 15% for having two R' nn atoms (for La doping [$x = 0.08$] the probabilities are 70%, 25%, and 7%, respectively). The differences between the corresponding subspectra, however, are too small to be resolved. Nevertheless, one has to keep in mind that by fitting the measured ^{57}Fe ME spectra with one component only, the obtained value of B_{hf} are values averaged over the different R' nn configurations and for that reason are smaller than those one would obtain for the configuration with one missing R' nn atom.

We have plotted in Fig. 5 the values of B_{hf} obtained from the ^{57}Fe ME spectra measured for $T \leqslant 10$ K and fitted as described earlier. A nonzero B_{hf} is found for T below 10 K for all three compounds. B_{hf} becomes zero at $T \approx 10$ K which is the Néel temperature T_N of *undoped* $DyNi_2B_2C$. In the case of Y and Lu doping it has been found that T_N is reduced to about 8 and 6 K, respectively. Since T_N is the temperature for long-range AF order and B_{hf} is a measure of short-range magnetic order (essentially only the nn rare earth atoms contribute to B_{hf}), we have to conclude that short-range magnetic correlations already exist above T_N. The extrapolated values of B_{hf} (0) differ for the three compounds, being the largest for Lu doping (about 0.4 T) and the smallest for Y doping (about 0.2 T). Since structural effects are almost negligible for Y doped samples (YNi_2B_2C and $DyNi_2B_2C$ have almost identical lattice parameters) we can conclude that the observed T_c reduction $\Delta T_c = 1$ K essentially is caused by the pair-breaking field which is of the order of $B_{\mathrm{hf}} \approx 0.2$ T or may be even much smaller if one averages the transferred or dipolar field B_{hf} over the superconducting coherence volume. This seems to be not unreasonable if one compares $\Delta T_c / B_{\mathrm{hf}} \approx 5$ K/T which is of the same order of magnitude as the measured reduction $|dT_c/dB_{\mathrm{ex}}| = 8$ K/T caused by an external field B_{ex} for $DyNi_2B_2C$ (Ref. 17). B_{hf} (0) for the La and Lu doped samples practically is the same and only slightly larger than that for Y doping. The reduction of T_c, on the other hand, is quite different for these two compounds compared to that for Y doping: $Dy_{0.92}La_{0.08}Ni_2B_2C$ and $Dy_{0.8}Lu_{0.2}Ni_2B_2C$ are *not* superconducting at all. It has been found that doping $DyNi_2B_2C$ with La and Lu, respectively, already destroys superconductivity at a La concentration of only 1% (Refs. 9 and 12), while T_c becoming zero for a Lu doping of about 15% (Ref. 1). Therefore, it is quite clear that the strong T_c reduction observed in these two systems is not caused by a pair-breaking field as it is the case for Y doping, but is due to the other magnetic effect (iv) suggested by Morozov.[2–4] In this case the T_c reduction is due to dilution of an AF superconductor with nonmagnetic atoms, which act as pair-breaking centers in the same way as paramagnetic impurities act in nonmagnetic superconductors. In order to understand the experimental results we have to conclude that the *strength* of this pair-breaking effect depends on the lattice distortion made by this nonmagnetic impurity. Freudenberger *et al.*[18] and G. Fuchs *et al.*[19] who studied in detail the influence of disorder on T_c in $R_{1-x}R'_xNi_2B_2C$ compounds essentially come to the same conclusion. La, therefore, which makes the largest distortions (see earlier) will be more effective in this pair-breaking effect than Lu. For Y doping, on the other hand, where the lattice distortions are negligible small, the T_c reduction can just be explained by the observed pair-breaking field, i.e., the T_c reduction due to effect (iv) seems to be quite small.

V. CONCLUSION

Dilution of the AF ordered superconductor $DyNi_2B_2C$ with nonmagnetic atoms R' ($R'=$Y, La, Lu) causes a reduc-

tion of T_c which is especially pronounced in the case of La. ^{57}Fe ME studies performed on the compounds $Dy_{0.8}R'_{0.2}Ni_2B_2C$ (R' = Y, Lu) and $Dy_{0.92}La_{0.08}Ni_2B_2C$ above and below $T_N \approx 10$ K give some information on the reasons for this T_c reduction. Whereas ^{57}Fe ME studies of pure $DyNi_2B_2C$ do not show any magnetic hf field B_{hf} at the ^{57}Fe(Ni) site even below T_N (Ref. 5), such a field exists for the magnetically diluted compounds. The magnitude of B_{hf} can explain the T_c reduction in the case of Y doping ($\Delta T_c \approx -1$ K) if one assumes that B_{hf} acts as a pair-breaking field in a similar way as an external field. The much stronger reduction of T_c for the Lu and La doped compounds (both are no longer superconductors), on the other hand, can be explained within the framework of Morozov[3] and demanding that this pair-breaking effect of nonmagnetic impurities is enhanced if the impurities distort the lattice.

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