Magnetic impurities in the pnictide superconductor $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$

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Abstract. Nuclear magnetic resonance (NMR) measurements have been performed on single crystals of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($x = 0, 0.45$) and $\text{CaFe}_2\text{As}_2$ grown from Sn flux. The Ba-based pnictide crystals contain significant amounts of Sn in their structure, $\sim 1\%$, giving rise to magnetic impurity effects evident in the NMR spectrum and in the magnetization. Our experiments show that the large impurity magnetization is broadly distributed on a microscopic scale, generating substantial magnetic field gradients. There is a concomitant 20% reduction in the transition temperature, which is most likely due to magnetic electron scattering. We suggest that the relative robustness of superconductivity ($x = 0.45$) in the presence of severe magnetic inhomogeneity might be accounted for by strong spatial correlations between impurities, such as clustering on the coherence length scale.

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1. Introduction

The new FeAs-based superconductors are interesting candidates for the study of competing magnetic and superconducting order. After the discovery of superconductivity \([1, 2]\) in electron-doped pnictides, their hole-doped counterparts were synthesized \([3, 4]\) with K-doped BaFe\(_2\)As\(_2\), Na-doped CaFe\(_2\)As\(_2\) \([5]\), as well as K- and Cs-doped SrFe\(_2\)As\(_2\) \([6, 7]\). The parent compounds for both the electron and hole-doped materials undergo structural phase transitions from tetragonal to orthorhombic on cooling, accompanied by an antiferromagnetic spin density wave (SDW) state. When the parent compounds are doped both the structural transition and the SDW are suppressed and superconductivity appears.

In fact, there is growing evidence for coexistence of static magnetism and superconductivity extending into the superconducting region of the FeAs-based superconductors. Muon spin relaxation (\(\mu\)SR) experiments \([8]–[10]\) in both electron and hole-doped pnictides have revealed some form of static magnetism in the superconducting state. A recent report on neutron diffraction in Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) showed that magnetism and superconductivity may coexist even up to 40% of K doping \([11]\). In order to understand the relationship between magnetism and superconductivity in the FeAs superconductors it is of central importance to determine if it is magnetic order or magnetic disorder that competes with superconductivity; whether the magnetism is local or exists in a separate phase, or is possibly isolated in various regions of the sample. This is the main thrust of our work where we use nuclear magnetic resonance (NMR) as a microscopic probe of magnetic impurities.

It is well established \([12]\) that s-wave superconductivity is suppressed by magnetic disorder where quasiparticle scattering from magnetic impurities is an effective pair breaking process, often called spin-flip scattering. In contrast, both potential and magnetic scattering in nons-wave superconductors are effective at breaking Cooper pairs \([13]\). Consequently, it is of interest to study the robustness of the superconducting state in the presence of magnetic impurities as compared to non-magnetic impurities. Additionally, impurities can play a key role in the pinning of flux, which may be essential in achieving high critical current densities in some applications.

We have investigated the effect of magnetic impurities in the normal state of crystals of the superconducting compound Ba\(_{0.55}\)K\(_{0.45}\)Fe\(_2\)As\(_2\), which we will refer to henceforth simply as BaK122, using \(^{75}\)As NMR (gyromagnetic ratio, \(\gamma = 7.2919\) MHz T\(^{-1}\)) (used as the reference for calculating the Knight shift in this work); spin, \(I = 3/2\); and natural abundance, 100%). We compare some of our results with undoped crystals, Ba122, and Ca122. The crystals were grown and characterized by Ni \textit{et al} \([4]\). The use of a Sn flux leads to \(\approx 1\%\) Sn impurity, that...
was suggested to reside on the As site, for Ba122 and BaK122 \[4\]. In contrast, the Ca122 crystals have negligible amounts of Sn in the structure \[14\]. The potassium-doped crystals become superconducting with a transition temperature of \(\sim 30\) K. By comparison with the pure compound \[3\] with the same doping we can infer that the \(T_c\) suppression is \(\sim 8\) K. The principal question we address is how uniformly distributed are these impurities and are they coupled to the conduction electrons. We have found that they are strongly magnetic; that they are locally distributed on a microscopic scale; and that they appear to be closely coupled to the conduction electrons. It is unusual that a compound remains superconducting in the presence of such significant amounts of magnetism.

Impurities play an important role in modifying the transition temperature and the amplitude of the order parameter in unconventional pairing systems and have been studied extensively in the case of \(^3\)He superfluid \[15\] and reviewed by Balatsky et al \[16\] for superconductors. In high-\(T_c\) cuprates NMR measurements of \(^{17}\)O in the Cu–O plane, and of the impurity ion itself, have been performed \[17\]. The cation substitution for planar copper of Zn \[18\], Ni \[19\], Li \[20\] in YBCO and Al substitution in LSCO \[21\] suppress \(T_c\) and create local moments. The fractional reduction in the transition temperature, \(\Delta T_c / T_c\) per % impurity (in the low concentration limit) for these examples \[18\]–\[23\] is, 0.036 (Ni), 0.12 (Zn), 0.058 (Li) and 0.5 (Al) which are similar to our sample of BaK122 with \(\sim 0.2\) (Sn) assuming \(\sim 1\%\) of Sn substituted into the structure. On the other hand, the magnetization of the BaK122 is almost two orders of magnitude larger than that of an LSCO sample with 3% impurity of Al for which superconductivity is completely eliminated.

Chemical substitution in the 122 family has a different role as compared with the cuprates in that superconductivity only appears by inhibiting the structural transition as can be achieved by insertion of Co into Ba122 \[24\], Sr122 \[25\] and Ni into Ba122 \[26\]. However, the nature and effect of impurity scattering on the superconducting state in the pnictides is not yet well established. Mössbauer spectroscopy has revealed \[27\] the presence of possible magnetic phases of FeAs, FeAs\(_2\) and Fe\(_2\)As in a significant amount. A zero-field NMR spectrum of \(^{75}\)As at \(\sim 265\) MHz in Sm oxypnictides \[28\] was attributed to the possible existence of some magnetic impurity phase. Although the \(\mu\)SR experiments \[8\]–\[10\] have identified static magnetism in both pnictides and oxypnictides, they could not ascertain its origin. A \(\mu\)SR measurement \[29\] on FeAs and FeAs\(_2\) seems to rule out the possibility of these two impurity phases as being responsible for the observed magnetism. In this paper, we report normal-state NMR measurements on crystals containing \(\sim 1\%\) Sn impurity of superconducting Ba\(_{0.55}\)K\(_{0.45}\)Fe\(_2\)As\(_2\) and non-superconducting BaFe\(_2\)As\(_2\) and CaFe\(_2\)As\(_2\).

2. Experimental methods

We have performed \(^{75}\)As NMR experiments from 6.4 to 14 T at Northwestern University and the National High Magnetic Field Laboratory for both of the Ba122 and BaK122 crystals at different temperatures from 40 to 180 K, with the \(c\)-axis parallel to the external magnetic field (\(H \parallel c\)). Several rectangular crystals were stacked along the crystallographic \(c\)-axis, and used for the NMR measurements corresponding to 10.6 mg for BaK122 and 11.5 mg for Ba122, having typical dimension of \(\sim 2 \times 2 \times 0.1\) mm\(^3\). All crystals were grown at Ames Laboratory and their magnetization measurements have been previously reported \[4\]. The NMR spectra were collected by a field sweep method, except for the spectra at 6.4 T, which were collected by frequency sweep. The temperature variation of the spectra for BaK122 was measured at
6.4 T and 62.21 MHz but only higher temperatures were used for the larger fields, 10–14 T. A typical $\pi/2$ pulse length was 1.8–2.5 $\mu$s, depending on experimental conditions, where we define this pulse length as one that maximizes the echo amplitude. The spin–lattice relaxation time ($T_1$) at 100 K at 8.5 T is $\sim$ 17 ms. There is a shift in the spectrum for the orientation $H \perp c$, indicating an anisotropic Knight shift, which we will not dwell upon here. A similar kind of anisotropy in the Knight shift has also been reported by Baek et al [30] for a Ba122 crystal grown by the Sn flux method.

3. Impurity effects on NMR

NMR measurements give both static and dynamic information about the local magnetic field and the electric field gradient distributions associated with impurities. The NMR spectrum can be shifted by local magnetic fields from an impurity magnetic moment, either through direct interactions via dipole–dipole coupling between local moments and the nucleus, or through indirect interactions involving hyperfine coupling to conduction electrons (indirect exchange) or orbital electrons (super exchange). The indirect interaction has an oscillatory character (see the review by Alloul [31], for example), which for dilute concentrations of impurities can be recognized from the magnitude of the effective field that they generate, defined later in this paper. Since the impurity effects associated with the indirect interaction are largely spatially inhomogeneous and are averaged over an effective field that is oscillatory, one typically finds significantly reduced paramagnetic shifts in the average local field displayed in the Knight shift [17]–[21]. On the other hand, the distribution of these shifts given by the NMR linewidth can be substantial. It is also well established that paramagnetic fluctuations from impurities can ‘wipe-out’ contributions to the NMR from nearby spectator nuclei owing to short spin–spin relaxation and/or short spin–lattice relaxation times.

4. Results and discussion

Figure 1 shows the full spectra for $H \parallel c$ and in more detail in figure 2, a representative selection from our data. We found the spacing between the satellite transition and the central transition, $\nu_Q$, to be $\sim$ 5 MHz.

We first discuss the parent Ba122 crystal measurements at temperatures above the structural transition comparing our results with those of [30] and [32]. Figure 2(a) shows the evolution of the spectra with magnetic field for Ba122. Our spectra have a double peak structure, more prominent above 100 K, also observed by Baek et al [30]. However, the full width at half-maximum (FWHM) of our broad peak is almost 4 times that of [30] (see figure 4). A weaker temperature-dependent magnetization was reported by Baek et al [30] compared to the present case [4], consistent with their narrower NMR line. However, the spectra reported by Kitagawa et al [32] are much narrower for their self-flux grown crystals as compared to Sn-flux grown crystals, and at 140 K consist of a single narrow line, having an FWHM of 3.5 kHz. The second-order quadrupolar broadening of the central transition should be zero for the $H \parallel c$ orientation, assuming that the asymmetry parameter $\eta = 0$. The central transition spectra for both doped and undoped crystals are too broad to be accounted for by misalignment. The Sn-flux grown samples are believed to have Sn impurities (of order 1%) incorporated in the crystal structure, which are responsible for its paramagnetism [4]. Kitagawa et al [32] have reported a significant increase in the linewidth for both the central and satellite transitions in Sn-flux grown Ba122 samples.

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having 1.5% Sn. They attributed this to disorder caused by Sn impurities. Baek et al [30] suggested that the broad line arises from an impurity phase, containing As, which they estimate to be about 40% of the total. The narrow line, or the ‘primary’ peak in their report, showed the existence of quadrupolar broadening (the linewidth decreases with increasing field). All of our data have substantial magnetic broadening. This indicates that there is a wide magnetic field distribution that persists to the nanometer scale, typical of magnetic interactions with the nuclear spin.

In order to investigate the origin of this broadening we have studied BaK122 crystals where magnetic ordering is believed to be suppressed by doping with potassium. The spectra are broader than for Ba122, and cannot be resolved into broad and narrow components, as was the case of Ba122. We have explored evolution of the spectra as a function of both temperature and magnetic field (a representative plot of the temperature evolution of the spectra at 62.21 MHz is shown in figure 2(b)) from which we conclude that the NMR line broadening is a result of static magnetic field distributions that become progressively more severe at

\[ \text{Figure 1.} \ ^{75}\text{As NMR spectra for the Ba122 and BaK122 crystals, obtained by field sweep. The uppermost trace is magnified by a factor of five to show the quadrupolar satellite transitions.} \]
lower temperatures, rendering the NMR line unobservable in the superconducting state. This is evident in figure 3, which shows the variation of the linewidth (FWHM), and the total nuclear magnetization (proportional to the number of resonating nuclei, given by the area of the spectrum) as a function of temperature at 62.21 MHz. The total nuclear magnetization deviates from the nuclear-Curie law below 80 K indicating that there is additional line broadening too large for us to fully observe the resonance. However, it is clear that the NMR linewidth, which is to say the magnetic field distribution, increases with decreasing temperature and increasing applied magnetic field. We note that the total nuclear magnetization for Ba122 also deviates from the nuclear-Curie law below 80 K in the SDW state.

The linear variation of the linewidth of the BaK122 spectra with magnetic field, measured at 100 K (figure 4), indicates that the linewidth is predominantly of magnetic origin. Figure 4 also shows the dependence on magnetic field of the linewidth of the broad and narrow components of the spectra for Ba122. The field dependence of the linewidth of the broad component is similar to that of BaK122, i.e. proportional to the magnetic field indicating that the origin of the line broadening is the same for both samples, and in particular for BaK122, this magnetic inhomogeneity coexists with the superconducting state since the NMR line remains too broad to observe below $T_c$.

We express the total linewidth phenomenologically as,

$$\Delta v = \Delta v_{\text{imp}} + \Delta v_{\text{intrinsic}},$$

Figure 2. Field sweep $^{75}$As NMR spectra (a) for the Ba122 at different Larmor frequencies at 100 K and (b) for BaK122 at different temperatures for the Larmor frequency 62.21 MHz. For both samples the line broadens with increasing field and decreasing temperature. The signal intensity decreases dramatically below 80 K and eventually become unobservable around 30 K (see figure 3). In panel (a), the dotted lines indicate a decomposition of the spectra into broad and narrow components.
Figure 3. Temperature dependence of $^{75}$As linewidth and the area (integral) of the spectra for BaK122 at the Larmor frequency 62.21 MHz. The solid line is the nuclear-Curie law fit expected for the NMR signal amplitude. We have also observed this deviation of the area of the spectra from the Curie law below 80 K for Ba122, a consequence of extreme magnetic NMR broadening. Error from the data analysis is indicated. Systematic error in the area measurement for $T > 80$ K is represented by the scatter in the data.

where $\Delta\nu_{\text{intrinsic}}$ is the intrinsic linewidth of the spectrum in the absence of magnetic inhomogeneity and for $^{75}$As, this would mostly be due to quadrupolar broadening. The fact that the linear fit in figure 4 passes through zero indicates that the quadrupolar contribution to the linewidth is negligible compared to the effect of magnetic impurities. In contrast, self-flux grown Ba122 crystals have a narrow NMR spectrum [32] and an absence of paramagnetic impurities. Based on the results in figure 4 for BaK122, we expect that $\Delta\nu$ should be proportional to the local magnetization $M(T, H_0)$, i.e. $\Delta\nu \propto M(T, H_0)$.

We have determined that the local magnetization is, in fact, closely related to the bulk magnetization [4], $\chi (T) H_0$. This is evident in figure 5, where we show that the NMR linewidth is proportional to the bulk magnetization. A Curie–Weiss-type temperature dependence of $\Delta\nu_{\text{imp}}$ is well known in the case of cation-doped YBCO [18]–[20] in $^{17}$O, $^{79}$Y and $^7$Li NMR and is also observed for $^{17}$O NMR in pure BSCCO crystals where in the later case the magnetic impurity has been associated with the oxygen dopant [33]. In general, doping with either magnetic or non-magnetic ions can lead to strong paramagnetism from local moments in cuprate superconductors for which the parent material is inherently magnetic.

The Knight shift, $K$, calculated from the first moment of the spectrum relative to the bare nucleus, can be expressed as

$$ K = K_{\text{para}} + K_s + K_{\text{orb}}, $$

where $K_s$ and $K_{\text{orb}}$ are the spin contribution from the mobile charge carriers and the orbital part of the Knight shift, respectively, and are expected to be temperature independent in the normal
Figure 4. Field dependence of $^{75}$As linewidth for BaK122 and Ba122 at 100 K. For Ba122 the spectra could be deconvolved into narrow and broad peaks (see figure 2). Data from Baek et al [30] for the Ba122 compound are also shown.

state. $K_{\text{para}}$ is the shift due to magnetic impurities and can be written as

$$K_{\text{para}} = \frac{1}{\mu_B} \chi(T) H_{\text{eff}}.$$  (3)

Here, $H_{\text{eff}}$ is the effective magnetic field at the As nucleus.

The data from all of our measurements have been plotted in figure 5, in the form $K_{\text{para}}H_0$ versus $\chi H_0$. From the linear fit to the total Knight shift at 6.4 T and 62.21 MHz we find $K_s + K_{\text{orb}}$ to be 0.37%, somewhat larger than for the undoped compound [32], 0.3%. The effective field we obtain from our fit is 5.3(1) kOe $\mu_B^{-1}$. If the magnetization from impurities were uniformly distributed then the effective field arising from direct dipolar coupling of the impurity moment to the $^{75}$As nuclei, based on $B = \mu_0 (H + 4\pi M)$, would be 0.6 kOe $\mu_B^{-1}$, an order of magnitude smaller than what we observe for the NMR shift shown in figure 5. Consequently, the effective field must be enhanced by hyperfine coupling and leads us to the conclusion that the As nuclei are indirectly coupled to the magnetic impurities through the conduction electrons, and therefore, the magnetic impurity resides in the FeAs conduction plane.

We cannot independently identify the magnetic contribution to depairing and determine its role in the suppression of $T_c$. However, we note that the resistivity in the normal state just above $T_c$ for BaK122 with $\approx$ 1% Sn impurity [4] is larger than for the pure compound [3] by $\sim 0.25$ m$\Omega$ cm, almost a factor of three; an impurity effect that is significantly larger than for 1% Zn substituted for Cu in YBCO$_2$ [23]. This suggests that the scattering mechanism for Sn in BaK122 might likely be identified with its comparatively larger magnetization and therefore be principally magnetic. So then it is puzzling why the transition temperature in BaK122 is only suppressed by $\sim 20\%$. One possible explanation might be that the magnetic impurity distribution, although very broad, might be strongly correlated, which is to say that
there are regions with fewer impurities on the coherence length scale that dominate the overall transition temperature via the proximity effect. Such correlation might result from clustering, for example. This phenomenon is well established [15] for fractally distributed impurities in superfluid $^3$He where it has been shown that the transition temperature is suppressed much less than the amplitude of the order parameter for a wide range of the strength of pair breaking.

Also in figure 5 we show the linewidth from the paramagnetically broadened NMR spectra as a function of $\chi H_0$. The effect of impurities is to produce a strongly inhomogeneous field distribution throughout the sample. In fact, as a point of comparison, consider the extreme model of a very inhomogeneous field distribution taken to be constant, up to a cutoff. In this case, the width of the distribution would be exactly half of the average. This situation is rather similar to our spectra for BaK122, as shown in figure 5, where the linewidth is twice the Knight shift. From this perspective it is evident that the magnetic field distribution is indeed very broad. Nonetheless, the absence of a narrow component in the spectrum indicates that the field distribution persists to the nanometer scale, typical of magnetic interactions with the nuclear spin.

All of our NMR experiments are based on the formation of a spin echo after two pulses, mostly involving the Fourier transform (FFT) of the echo. Ideally the pulses are a $\pi/2 - \tau - \pi - \tau$ – echo sequence (Hahn echo). During the time $2\tau$, development of spin decoherence reduces the echo amplitude and, in principle, can alter the shape of the FFT spectrum. Decoherence is determined by spin–spin relaxation for which an example is shown in figure 6. Here we compare the relaxation profiles for the crystals of BaK122 and Ca122, above the temperature for the structural transition for the latter. Additionally, we show the echo amplitude evolution in
BaK\(_{122}\) using the CPMG sequence \((\pi/2)_x - \tau - \pi_y - \tau - \text{echo} - \tau - \pi_y - \ldots\) where the indices \(x, y\) label RF pulses with orthogonal phases (see for example, [35]).

For a static, homogeneous environment of the nuclear spin its spin–spin relaxation time, \(T_2\), should be less than that determined by the nuclear dipole–dipole coupling. From the crystal structure we calculate that \(T_2\) from this coupling is 0.72 ms for BaK\(_{122}\), and 0.59 ms for Ca\(_{122}\), which has negligible impurities. The calculated \(T_2\) is close to what we observe in the case of the Ca\(_{122}\) crystal. However, for BaK\(_{122}\) the recovery profile gives a larger \(T_2\) than expected by \(\approx 2.5\), for small \(2\tau\) values. This result indicates that there is quenching of the dipole–dipole interaction for BaK\(_{122}\), presumably from magnetic field gradients producing local field differences greater than the dipolar field of the near-neighbor As atoms. We were then led to explore whether these field gradients were dynamic by application of a CPMG sequence that can reduce or eliminate their stochastic effect [34]. Indeed, the CPMG recovery profile develops even less rapidly than that for the Hahn echo, suggestive of the existence of these field fluctuations. Theoretical analysis [34] of the Hahn echo profile gives the fit shown in figure 6 for a characteristic field fluctuation frequency \((\omega)\) of just 2.2 kHz, and with an amplitude of 4.8 G. Although the fit is excellent, we should be careful about this interpretation since there is not a well-defined \(\pi\)-pulse. The RF-pulses are rather inhomogeneous over the sample and, secondly, the NMR line for BaK\(_{122}\) is very broad, meaning that much of the received signal is off-resonance. In this regard, we note that the CPMG experiment on Ca\(_{122}\) for which the crystal has a similar geometry and consequently the same inhomogeneous RF-field, has a CPMG recovery profile, which is the same as for the Hahn echo. This is consistent with our expectation for a pure compound in the absence of field fluctuations. A similar effect was observed in
$^{195}$Pt NMR in nanometer size unsupported Pt particles [35]. There the Hahn-echo $T_2$ of the Pt nuclei on the particle surface is much shorter than the CPMG $T_2$, which can be accounted for by an inhomogeneous magnetic field with field fluctuations arising from spin-diffusion. If the local fields are indeed fluctuating in BaK122 in the kHz range, this is so low in frequency that it suggests that the magnetism is a collective phenomenon, possibly superparamagnetic, rather than being associated with independent fluctuations of local moments. Most importantly however, is that we have found an unusually long $T_2$, which is expected for large local magnetic field gradients in BaK122.

We have also compared spin–lattice relaxation in BaK122 and in Ca122. For the former we find $T_1$ at 100 K $\sim$ 17 ms, in comparison with 7.6 ms at 190 K for Ca122. The $T_1$ for BaK122 is comparable to the $T_1$ in Ba122 reported in [30] at the same temperature. Despite the existence of magnetic impurities in BaK122, its relatively long $T_1$ gives no indication for a contribution to spin–lattice relaxation from field fluctuations, possibly because their frequency is too low compared to the Larmor frequency. Lastly, it is essential in an NMR experiment to check how much of the sample is contributing to the signal. It is meaningless to interpret NMR results if the vast majority of the sample, relevant in comparisons with other experiments, does not contribute to the NMR signal. We have made a direct estimate of the NMR active fraction of the samples comparing BaK122 and Ca122 and have found that the NMR signal strength is comparable, taking sample shape and size into account and using the same NMR conditions. Consequently, we believe that the results we report are representative of the entire sample with the exception, as noted above, of data below 80 K in BaK122 and Ba122.

5. Summary

The magnetization from impurities in our BaK122 crystals, grown from Sn flux, is exceptionally large. In fact the magnetization is $\sim$ 60 times larger than that of La$_{1.85}$Sr$_{0.15}$CuO$_4$ for which superconductivity is completely suppressed by Al substitution. The large Curie–Weiss-like magnetization in BaK122 results in a significant broadening and displacement of the $^{75}$As NMR spectrum. Since there is no narrow component we infer that the magnetic inhomogeneity persists to a microscopic scale. The local moments associated with these impurities appear to be coupled to the As nucleus by an indirect interaction through the conduction holes with an effective field $H_{\text{eff}} \sim 5$ kOe $\mu_B^{-1}$. This result shows that the magnetic impurities reside in the FeAs conduction plane, consistent with the claim by Ni et al [4] that Sn substitutes for As in the structure. Superconductivity in BaK122 takes place in a backdrop of inhomogeneous magnetism associated with these impurities. The extent of pair breaking from magnetic impurity scattering can only be qualitatively linked to their paramagnetism, or possibly superparamagnetism. Nonetheless, our BaK122 crystals are indeed superconducting and exhibit a relative suppression of the transition temperature of only 20%. We attribute the robustness of superconductivity in the presence of magnetic impurities to strong spatial correlations between the impurities, a non-uniformity that is also apparent in the large magnetic field distributions and field gradients which we observe directly with NMR.

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