Cosmic rays are particles (mostly protons) accelerated to relativistic speeds. Despite wide agreement that supernova remnants (SNRs) are the sources of galactic cosmic rays, unequivocal evidence for the acceleration of protons in these objects is still lacking. When accelerated protons encounter interstellar material, they produce neutrons, which in turn decay into gamma rays. This offers a compelling way to detect the acceleration sites of protons. However, the presence of relativistic protons in SNRs has been mostly inferred from indirect arguments (2–5).

A direct signature of high-energy protons is provided by gamma rays generated in the decay of neutral pions ($\pi^0$); proton-proton (more generally nuclear-nuclear) collisions create $\pi^0$ mesons, which usually quickly decay into two gamma rays ($\gamma + \gamma$)– schematically written as $p + p \rightarrow \pi^0 + \text{other products}$, followed by $\pi^0 \rightarrow 2\gamma$), each having an energy of $m_{\pi^0}/2 = 67.5$ MeV in the rest frame of the neutral pion (where $m_{\pi^0}$ is the rest mass of the neutral pion and $c$ is the speed of light). The gamma-ray number spectrum, $\Gamma(\gamma)$, is thus symmetric about 67.5 MeV (10).

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interacting with molecular clouds are the most luminous SNRs in gamma rays (11, 12). The best examples of SNR-cloud interactions in our galaxy are the SNRs IC 443 and W44 (13), which are the two highest-significance SNRs in the second Fermi Large Area Telescope (LAT) catalog (2FGL) (14) and are thus particularly suited for a dedicated study of the details of their gamma-ray spectra. The age of each remnant is estimated to be ~10,000 years. IC 443 and W44 are located at distances of 1.5 kpc and 2.9 kpc, respectively.

We report here on 4 years of observations with the Fermi LAT (4 August 2008 to 16 July 2012) of IC 443 and W44, focusing on the sub-GeV part of the gamma-ray spectrum—a crucial spectral window for distinguishing the d0-decay gamma rays from electron bremsstrahlung or inverse Compton scattering produced by relativistic cosmic rays from electron bremsstrahlung or inverse Compton scattering produced by relativistic cosmic rays. Note that the gamma-ray rejection (so-called Pass 7) provides an increase were limited to the energy band above 200 MeV, mainly because of the small and rapidly changing LAT effective area at low energies. A recent update to the event classification and background subtraction (so-called Pass 7) provides an increase in LAT effective area at 100 MeV by a factor of ~5 (18), enabling the study of bright, steady sources in the galactic plane below 200 MeV with the Fermi LAT. Note that the gamma-ray spectral energy distribution of W44 measured recently by the AGILE satellite falls steeply below 1 GeV, which the authors interpreted as a clear indication for the d0-decay origin of the gamma-ray emission (19). Also, a recent analysis of W44 at high energies (above 2 GeV) has been reported (20), revealing large-scale gamma-ray emission attributable to high-energy protons that have escaped from W44. Here, we present analyses of the gamma-ray emission from the compact regions delineated by the radio continuum emission of IC 443 and W44.

The analysis was performed using the Fermi LAT Science Tools (21). We used a maximum likelihood technique to determine the significance of a source over the background and to fit spectral parameters (22, 23). For both SNRs, additional sources seen as excesses in the background-subtracted map have been added to the background model (24) and are shown as diamonds in Fig. 1— one in the case of IC 443, three in the case of W44. The inclusion of these sources had no influence on the fitted spectrum of the SNRs. Three close-by sources (2FGL J1582.0–0156c, 2FGL J1587.2+0055c, and 2FGL J1588.5+0129c) have been identified with escaping cosmic rays from W44 (20). These 2FGL sources have been removed from the background model (see below) in order to measure the full cosmic-ray content of W44.

Figure 2 shows the spectral energy distribution obtained for IC 443 and W44 through maximum likelihood estimation. To derive the flux points, we performed a maximum likelihood fitting in 24 independent logarithmically spaced energy bands from 60 MeV to 100 GeV. The normalization of the fluxes of IC 443 and W44, and those of neighboring sources and of the galactic diffuse model, was left free in the fit for each bin. In both sources, the spectra below ~200 MeV are steeply rising, clearly exhibiting a break at ~200 MeV. To quantify the significance of the spectral breaks, we fit the fluxes of IC 443 and W44 between 60 MeV and 2 GeV—below the high-energy breaks previously found in the 1-year spectra (15, 16)—with both a single power law of the form \( F(E) = K(E/E_0)^{-\gamma} \) and a smoothly broken power law of the form \( F(E) = K(E/E_0)^{-\gamma} + (E/E_0)^{-\beta} \) with \( E_0 = 200 \text{ MeV} \). The spectral index changes from \( \Gamma_1 \) to \( \Gamma_2 (>\Gamma_1) \) at the break energy \( E_B \). The smoothness of the break is determined by the parameter \( \alpha \), which was fixed at 0.1 (Table 1). We define the test-statistic value \( Z^2 \) as \( 2 \ln L_{\text{break}} \), where \( L_{\text{break}} \) corresponds to the likelihood value for the source/no-source hypothesis (24). The detection significance is given by \( Z^2 \). The smoothly broken power law model yields a significantly larger \( Z^2 \) than a single power law, establishing the existence of a low-energy break. The improvement in log likelihood when comparing the broken power law model to a single power law corresponds to a formal statistical significance of 19σ for the
low-energy break in IC 443 and 21r for that in W44, when assuming a nested model with two additional degrees of freedom.

To determine whether the spectral shape could indeed be modeled with accelerated protons, we fit the LAT spectral points with a $\pi^0$-decay spectral model, which was numerically calculated from a parameterized energy distribution of relativistic protons. Following previous studies (15, 16), the parent proton spectrum as a function of momentum $p$ was parameterized by a smoothly broken power law in the form of

$$\frac{dN}{dp} \propto p^{-s_1} \left[ 1 + \left( \frac{p}{p_b} \right)^{s_2} \right]^{-\gamma}$$

Best-fit parameters were searched using $\chi^2$-fitting to the flux points. The measured gamma-ray spectra, in particular the low-energy parts, matched the $\pi^0$-decay model (Fig. 2). Parameters for the underlying proton spectrum are $s_1 = 2.36 \pm 0.02$, $s_2 = 3.1 \pm 0.1$, and $p_b = 239 \pm 74$ GeV cm$^{-2}$ for IC 443, and $s_1 = 2.36 \pm 0.05$, $s_2 = 3.5 \pm 0.3$, and $p_b = 22$ GeV cm$^{-2}$ for W44 (statistical errors only). In Fig. 3 we show the energy distributions of the high-energy protons derived from the gamma-ray fits. The break $p_b$ is at higher energies and is unrelated to the low-energy pion-decay bump seen in the gamma-ray spectrum. If the interaction between a cosmic-ray precursor (i.e., cosmic rays distributed in the shock upstream on scales smaller than $\sim 0.1R$, where $R$ is the SNR radius) and adjacent molecular clouds were responsible for the bulk of the observed GeV gamma rays, one would expect a much harder energy spectrum at low energies (i.e., a smaller value for the index $s_1$), contrary to the Fermi observations. Presumably, cosmic rays in the shock downstream produce the observed gamma rays; the first index $s_1$ represents the shock acceleration index with possible effects due to energy-dependent propagation, and $p_b$ may indicate the momentum above which protons cannot be effectively confined within the SNR shell. Note that $p_b$ results in the high-energy break in the gamma-ray spectra at $\sim 20$ GeV and $\sim 2$ GeV for IC 443 and W44, respectively.

The $\pi^0$-decay gamma rays are likely emitted through interactions between “crushed cloud” gas and relativistic protons, both of which are highly compressed by radiative shocks driven into molecular clouds that are overtaken by the blast wave of the SNR (25). Filamentary structures of synchrotron radiation seen in a high-resolution radio continuum map of W44 (26) support this picture. High-energy particles in the “crushed cloud” can be explained by reacceleration of the preexisting galactic cosmic rays (25) and/or freshly accelerated particles that have entered the dense region (20). The mass of the shocked gas...
(\(-1 \times 10^7 M_\odot\) and \(-5 \times 10^3 M_\odot\) for IC 443 and W44, respectively, where \(M_\odot\) is the mass of the Sun) is large enough to explain the observed gamma-ray luminosity. Because the “crushed cloud” is geometrically thin, multi-GeV particles are prone to escape from the dense gas, which may explain the break \(p_{br}\).

Escaped cosmic rays reaching the unshocked molecular clouds ahead of the SNR shock can also produce \(n^-\)-decay gamma rays (27, 28). Indeed, the gamma rays emitted by the escaped cosmic rays in the large molecular complex that surrounds W44 (total extent of 100 pc) have been identified with three close-by sources (29), which led us to remove them from the model in the maximum likelihood analysis, as mentioned above. With this treatment, the measured fluxes below 1 GeV contain small contributions from the escaped cosmic rays, but this does not affect our conclusions. The escaped cosmic rays may significantly contribute to the measured TeV fluxes from IC 443 (29, 30). Emission models could be more complicated. For example, the cosmic-ray precursor with a scale of \(-0.1R\) at the highest energy could interact with the adjacent unshocked molecular gas, producing hard gamma-ray emission. This effect is expected to become important above the LAT energy range.

We should emphasize that radiation by relativistic electrons cannot account for the gamma-ray spectra of the SNRs as naturally as radiation by relativistic protons can (23). An inverse-Compton origin of the emission was not plausible on energetic grounds (11). The most important seed photon population for scattering is the infrared radiation produced locally by the SNR itself, with an energy density of \(-1\) eV \(\text{cm}^{-3}\), but this is not large enough to explain the observed gamma-ray emission. Unless we introduce in an ad hoc way an additional abrupt break in the electron spectrum at 300 MeV (Fig. 2, dash-dotted lines), the bremsstrahlung models do not fit the observed gamma-ray spectra. If we assume that the same electrons are responsible for the observed synchrotron radiation in the radio band, a low-energy break is not expected to be very strong in the radio spectrum, and thus the existing data do not rule out this scenario. The introduction of the low-energy break introduces additional complexity, and therefore a bremsstrahlung origin is not preferred. Although most of the gamma-ray emission from these SNRs is due to \(n^-\) decay, electron bremsstrahlung may still contribute at a lower level. The Fermi LAT data allow an electron-to-proton ratio \(K_{ep}\) of \(-0.01\) or less, where \(K_{ep}\) is defined as the ratio of \(dn\_e/d\alpha\) and \(dn\_p/d\alpha\) at \(\rho = 1\) GeV \(c^{-1}\) (figs. S2 and S3).

Finding evidence for the acceleration of protons has long been a key issue in attempts to elucidate the origin of cosmic rays. Our spectral measurements down to 60 MeV enable identification of the \(n^-\) decay feature, thus providing direct evidence for the acceleration of protons in SNRs. The proton momentum distributions, well constrained by the observed gamma-ray spectra, are yet to be understood in terms of acceleration and escape processes of high-energy particles.

Table 1. Spectral parameters in the energy range of 60 MeV to 2 GeV for power-law (PL) and broken power-law (BPL) models. \(TS = 2 \ln(L/L_{0})\) is the test-statistic value.

<table>
<thead>
<tr>
<th>Model</th>
<th>(K) (cm(^2) s(^{-1}) MeV(^{-1}))</th>
<th>(\Gamma_1)</th>
<th>(\Gamma_2)</th>
<th>(K_{be}) (MeV)</th>
<th>(TS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IC 443</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL</td>
<td>(11.7 \pm 0.2) (\times 10^{-10})</td>
<td>(1.76 \pm 0.02)</td>
<td>---</td>
<td>---</td>
<td>21,651</td>
</tr>
<tr>
<td>BPL</td>
<td>(11.9 \pm 0.6) (\times 10^{-10})</td>
<td>(0.57 \pm 0.25)</td>
<td>(1.95^{+0.02}_{-0.01})</td>
<td>245(^{+16}_{-15})</td>
<td>22,010</td>
</tr>
<tr>
<td>W44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PL</td>
<td>(13.0 \pm 0.4) (\times 10^{-10})</td>
<td>(1.71 \pm 0.03)</td>
<td>---</td>
<td>---</td>
<td>6,920</td>
</tr>
<tr>
<td>BPL</td>
<td>(15.8 \pm 1.0) (\times 10^{-10})</td>
<td>(0.07 \pm 0.4)</td>
<td>(2.08^{+0.01}_{-0.03})</td>
<td>253(^{+11}_{-11})</td>
<td>7,351</td>
</tr>
</tbody>
</table>

Fig. 3. Proton and gamma-ray spectra determined for IC 443 and W44. Also shown are the broadband spectral flux points derived in this study, along with TeV spectral data points for IC 443 from MAGIC (29) and VERITAS (30). The curvature evident in the proton distribution at ~2 GeV is a consequence of the display in energy space (rather than momentum space). Gamma-ray spectra from the protons were computed using the energy-dependent cross section parameterized by (32). We took into account accelerated nucleii (heavier than protons) as well as nuclei in the target gas by applying an enhancement factor of 1.85 (32). Note that models of the gamma-ray production via pp interactions have some uncertainty. Relative to the model adopted here, an alternative model of \(6\) predicts ~30% less photon flux near 70 MeV; the two models agree with each other to better than 150% above 200 MeV. The proton spectra assume average gas densities of \(n = 20\) cm\(^{-3}\) (IC 443) and \(n = 100\) cm\(^{-3}\) (W44) and distances of 1.5 kpc (IC 443) and 2.9 kpc (W44).

References and Notes
15. A. A. Abd et al., Science 327, 2123 (2010).
21. http://fermi.gsfc.nasa.gov/ssc/32. The region model fitted to the data includes the SNR of interest (IC 443 or W44), background point sources from the 2FGL catalog (14), the galactic diffuse emission (ring_Zygiel_P7V6_source_v0810), and a corresponding isotropic component (isotropic_Zygiel_P7V6_source_v0810).
23. See supplementary materials on Science Online.
Crystalline Inorganic Frameworks with 56-Ring, 64-Ring, and 72-Ring Channels

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The development of zeolite-like structures with extra-large pores (>12-membered rings, 12R) has been sporadic and is currently at 30R. In general, templating via molecules leads to crystalline frameworks, whereas the use of organized assemblies that permit much larger pores produces noncrystalline frameworks. Synthetic methods that generate crystallinity from both discrete templates and organized assemblies represent a viable design strategy for developing crystalline porous inorganic frameworks spanning the micro and meso regimes. We show that by integrating templating mechanisms for both zeolites and mesoporous silica in a single system, the channel size for gallium zincophosphites can be systematically tuned from 24R and 28R to 40R, 48R, 56R, 64R, and 72R. Although the materials have low thermal stability and retain their templating agents, single-activator doping of Mn$^{2+}$ can create white-light photoluminescence.

Crystalline open-framework materials are of interest because of their rich structural chemistry and their use ranging from conventional catalysis, gas separation, and ion exchange to modern high-tech low-k materials, zeolite-dye microlasers, high-capacity H$_2$ and CO$_2$ gas storage (1–4), and potential lanthanide-free phosphor materials for light-emitting diodes (5–7). Their functions are mainly attributed to properties related to pore size. Therefore, pore engineering goals such as enlarging the channels, changing channel shape and connectivity, or modifying the wall composition are critical for creating new materials.

For many years, various zeolite-like structures have been synthesized using both simple and complex preparative techniques. In 1982, the discovery of AlPO$_4$-based zeolite structures (8) inspired the synthesis of open-framework metal phosphates. Soon after, the crystal structure of an iron phosphate mineral known as cacoxenite (9) was solved, revealing that the structure contained notably large channels with a free diameter of 1.4 nm and openings encircled by 36 polyhedra (36R). These discoveries led to increasing interest in pure tetrahedral and mixed polyhedral frameworks with extra-large channels (table S1). Later, many landmark structures were synthesized.

Fig. 1. Systematic expansion of structures with extra-large channels. (A) Channel ring size ranging from 24R to 72R. (B) Pore diameters spanning the micro and meso regimes. The templates are alkyl monoamines (using a ball-and-stick model) with carbon chain lengths ranging from 4C to 18C.