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Acidic Lakes and Streams in the United States: The Role of Acidic Deposition

LAWRENCE A. BAKER, ALAN T. HERLIHY, PHILIP R. KAUFMANN, JOSEPH M. EILERS

A statistically designed survey of lakes and streams conducted by the Environmental Protection Agency in acid-sensitive areas of the United States, the National Surface Water Survey (NSWS), was used to identify the role of acidic deposition relative to other factors in causing acidic conditions in an estimated 1180 lakes and 4670 streams. Atmospheric deposition was the dominant source of acid anions in 75 percent of the acidic lakes and 47 percent of the acidic streams. Organic anions were dominant in one-fourth of the acidic lakes and streams; acidic mine drainage was the dominant acid source in 26 percent of the acidic streams. Other causes of acidic conditions were relatively unimportant on a regional scale. Nearly all the deposition-dominated acidic systems were found in six well-delineated subpopulations that represent about one-fourth of the NSWS lake population and one-third of the NSWS stream population.

There is now little question that acidic deposition can cause surface water acidification (1), although many surface waters are acidic for reasons unrelated to acidic deposition, such as acidic drainage from mine tailings or natural production of organic acids. Thus, a major policy question regarding emissions reductions is: What is the role of acidic deposition, in relation to other factors, in the occurrence and distribution of acidic (2) waters in the United States?

If adequate historical data were available, determining the role of acidic deposition would be reasonably straightforward. But historical water quality data are sparse, questions regarding comparability of data are often unresolvable, and exogenous factors may have contributed to observed changes (3). Consequently, with a few exceptions, studying the direct association between long-term (>10 years) water quality trends and deposition trends has not been a productive approach for assessment of acidification on a regional scale. Paleolimnological research has been valuable, particularly in the Adirondacks, where a statistically designed study has been used to make a quantitative assessment of historical acidification (4, 5); in other regions, too few lakes have been studied to make quantitative regional assessments. Thus, in this paper, we base our assessment of the causes of acidic conditions largely on inferences from current chemical composition (6).

Our analysis is based on the Environmental Protection Agency's National Surface Water Survey (NSWS), a statistically designed synoptic survey of lakes and streams conducted in acid-sensitive areas of the United States (7, 8) (Fig. 1). We segregated acidic NSWS surface waters into three subpopulations: (i) organic-dominated surface waters, in which organic anions (Ap) exceed SO4\(^{2-}\) on an equivalent basis (9), (ii) waters dominated by watershed sources of sulfate, in which measured SO4\(^{2-}\) concentrations are more than twice as high as concentrations predicted from evapoconcentration of atmospheric inputs (10), and (iii) deposition-dominated waters, in which SO4\(^{2-}\)+NO3\(^{-}\) from atmospheric deposition are the dominant acid anions. Although Cl\(^{-}\) is a strong acid anion and is important in coastal areas of the NSWS, we did not identify a chloride-dominated class because chloride generally enters watersheds as a neutral salt (sea spray or road salt), rather than as HCl.

The deposition-dominated group includes 75% of the acidic lakes and 47% of the acidic streams in the NSWS (Table 1). Within this group, 67% of the lakes and 88% of the streams had SO4\(^{2-}\):(Cl\(^{-}\)) ratios greater than 1.0 (11) (C, is base cations). Ratios greater than 1.0 imply that H2SO4 inputs exceed the capacity of watersheds to neutralize acid inputs by C, production (12). Therefore, H2SO4 inputs alone are sufficient to cause acidic conditions in most acidic deposition-dominated surface waters in the NSWS. Deposition-dominated, acidic surface waters typically had SO4\(^{2-}\) concentrations of 70 to 150 μg/liter, and low concentrations of NO3\(^{-}\) and dissolved organic carbon (DOC) (Table 1). For 97% of the streams and 60% of the lakes in this category, [A\(^{-}\)] is less than 20% of [SO4\(^{2-}\) + NO3\(^{-}\)].

One-fourth of both the acidic lakes and the acidic streams are organic-dominated (Table 1). Most of these are naturally acidic, indicated by the observation that half the lakes and 75% of the streams in this category had A\(^{-}\):(C, + Cl\(^{-}\)) ratios greater than 1.0 (13). Lakes and streams in this group had much higher DOC and lower SO4\(^{2-}\) than those in the deposition-dominated category (Table 1). This difference reflects the more frequent occurrence of wetlands in watersheds of the organic-dominated systems (14). In all, 80% of the organic-dominated acidic lakes are in Florida and the Upper Midwest; all sampled acidic streams in this category are in the Mid-Atlantic Coastal Plain and Florida.

One-fourth of the acidic NSWS streams are in the watershed sulfate-dominated category; nearly all these streams are acidic because of mine drainage. Sulfate and C, + Cl\(^{-}\) were typically much higher in these streams than in deposition-dominated streams (Table 1). There was evidence of mining activity in every mine drainage stream watershed, and many had characteristic “yellow boy” (iron hydroxide) deposits. In the NSWS, streams impacted by acidic mine drainage were found primarily in the coal mining region of the Mid-Atlantic Highlands (15). Only 3% of the acidic lakes are in the watershed sulfate-dominated category (Table 1) (16).

Nearly all the deposition-dominated acidic NSWS lakes and streams were found in six well-delineated subpopulations (Fig. 1 and Table 2). The two NSWS subpopulations most clearly affected by acidic deposition are lakes in the southwest Adirondack Mountains and lakes and streams in forested watersheds of the Mid-Atlantic Highands.

All acidic NSWS lakes in the Adirondacks are located in the southwestern third of the subregion. Most are rapidly flushed drainage systems; sensitivity to acidification in this region is controlled largely by depth of overlying glacial till and bedrock type (17). Paleolimnological studies (5, 18) in this region have shown that although some lakes were naturally acidic, the number of acidic lakes has tripled since preindustrial times, with concomitant increases in levels of inor-
For deposition-dominated acidic streams, nearly all deposition-dominated and have \(SO_4^{2-} : (C_{B} - Cl^-)\) ratios greater than 1.0 have become more acidic since preindustrial times. Thus, paleolimnological studies corroborate inferences from lake chemistry.

Nearly all deposition-dominated acidic streams and lakes in the Mid-Atlantic Highlands are in forested watersheds with areas less than 30 km\(^2\) and at elevations greater than 300 m; waters in lowland valleys are well buffered. Reliable historical data documenting acidification caused by acidic deposition in this region are sparse. However, for deposition-dominated acidic streams, \(SO_4^{*}\) and Al concentrations were high (mean of 148 \(\mu\)g/liter and 202 \(\mu\)g/liter, respectively), and \(A^-\) concentrations were low (mean of 10 \(\mu\)g/liter). Thus, the current chemical composition overwhelmingly implicates deposition-induced acidification.

Acidic NSWS lakes in New England are a heterogeneous population, and watershed cultural disturbances complicate geochemical interpretations for many lakes. Most acidic lakes in this subpopulation are deposition-dominated; about half had \(SO_4^{*} : (C_{B} - Cl^-)\) ratios >1.0 (Table 2). Paleolimnological studies in lakes that have acidified indicate that the timing of acidification coincides with increases in fossil fuel combustion (19).

Nearly all (93%) deposition-dominated acidic lakes in the Upper Midwest are low-silica lakes. Most are seepage lakes (defined as lakes with no mapped inlets or outlets) located in the eastern part of the region (Fig. 1). Here, silica concentration is a surrogate for ground-water input, which in turn determines sensitivity to acidification (20). The acidification signal is not as strong here as in other regions: 82% of the acidic lakes in this group are deposition-dominated, but in half of these, \([A^–]\) constituted more than 30% of \([SO_4^{*} + NO_3^-]\). Historical surveys and paleolimnological studies show that pH and ANC have declined in a few lakes, although pH and ANC have increased in many lakes whose watersheds have been disturbed (21).

In Florida, 94% of the deposition-dominated acidic lakes and all sampled deposition-dominated acidic streams are in the northern highlands area (22) (Fig. 1). Most of these had low DOC (<3 mg/liter). Paleolimnological data indicate that recent acidification has occurred in the northern peninsula of Florida, but some deposition-dominated acidic lakes in the Panhandle appear to be naturally acidic (23).

The sixth area of interest is the Atlantic Coastal Plain. Although many streams in this area are organic-dominated, there is also a substantial population of deposition-dominated acidic streams, mainly in the Pine Barrens of New Jersey. Of perhaps greater interest than acidic streams in the Coastal Plain are the many nonacidic streams with pH less than 6.0, about half the population. These streams are an important resource for anadromous fish, which are particularly sensitive to acid stress. Although evidence of fish loss due to acidification in this region is inconclusive, over half the streams had acid-base chemistry unsuitable (low pH, high aluminum, low calcium) for sensitive indigenous species, such as blueback herring (24).

Taken together, these six high-interest subpopulations represent about one-fourth of the lake population and one-third of the stream population in the NSWS, but they include nearly all the deposition-dominated acidic surface waters (95% of the lakes and 84% of the streams). In several areas of the NSWS, few acidic systems were found. No acidic lakes were sampled in Minnesota; only one acidic lake, affected by a geothermal spring, was sampled in the West; and less than 2% of the lakes and streams sampled in the Interior Southeast were acidic (Fig. 1).

We examined only three potential causes of acidic conditions, but it is unlikely that other mechanisms are important on a regional scale. Among other possible causes, forest regrowth following cutting in the early 1900s has been the most widely debated (5, 25-27). However, in the Adirondacks, where paleolimnological studies are most complete, the timing of acidification corresponds better with the increase in industrial emissions than with forest cutting and regrowth (27). Furthermore, there is no evidence that forest regrowth has caused surface waters to become acidic in regions with low \(SO_4^{2-}\) deposition.

Retention of sea-salt cations (28) is probably unimportant as a cause of chronic acidic conditions in Northeast coastal lakes and Mid-Atlantic streams, and it is a minor contributor of \(H^+\) in low-ANC waters in Florida (29); however, short-term acidification caused by retention of marine salts during storms is well documented in coastal areas (30). Hydrologic changes, such as droughts, can have a profound effect on acid-base chemistry (31), but there is no evidence that long-term hydrologic change alone has increased the number of acidic surface waters on a regional scale.

### Table 1. Characteristics (medians) of acidic NSWS lakes and streams, by chemical class. All units are in microequivalents per liter, except DOC, which is in milligrams per liter; \(N\) is the estimated number of acidic lakes and streams in the NSWS target population; stream data are for upstream ends of reaches.

<table>
<thead>
<tr>
<th>Chemical dominance</th>
<th>(N)</th>
<th>(SO_4^*)</th>
<th>(NO_3^-)</th>
<th>DOC</th>
<th>(A^-)</th>
<th>(C_B - Cl^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition</td>
<td>881</td>
<td>102</td>
<td>1.0</td>
<td>2</td>
<td>15</td>
<td>83</td>
</tr>
<tr>
<td>Lakes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Streams</td>
<td>2190</td>
<td>117</td>
<td>2.4</td>
<td>2</td>
<td>11</td>
<td>86</td>
</tr>
<tr>
<td>Organic acids</td>
<td>260</td>
<td>27</td>
<td>0.9</td>
<td>11</td>
<td>78</td>
<td>57</td>
</tr>
<tr>
<td>Lakes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Streams</td>
<td>1250</td>
<td>44</td>
<td>0.5</td>
<td>25</td>
<td>179</td>
<td>128</td>
</tr>
<tr>
<td>Watershed sulfate</td>
<td>39</td>
<td>419</td>
<td>0.3</td>
<td>6</td>
<td>41</td>
<td>610</td>
</tr>
<tr>
<td>Lakes</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Streams</td>
<td>1230</td>
<td>3520</td>
<td>1.2</td>
<td>1</td>
<td>6</td>
<td>3110</td>
</tr>
</tbody>
</table>
Table 2. High-interest subpopulations in the NSWS. These were developed using physiographic maps, land-use data, and chemical data in an attempt to narrowly circumscribe deposition-dominated acidic lakes and streams (8). Streams were not sampled in the Adirondacks, New England, or the Upper Midwest. A dash indicates that there were no sampled systems in that category.

<table>
<thead>
<tr>
<th>Subpopulation</th>
<th>$N$</th>
<th>Percent of total</th>
<th>Deposition (%)</th>
<th>Organic (%)</th>
<th>Watershed-S (%)</th>
<th>SO$_4^{2-}$: (C$_n$ – C) &gt; 1 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SW Adirondack lakes*</td>
<td>176</td>
<td>38</td>
<td>100</td>
<td>13</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>New England lakes</td>
<td>207</td>
<td>5</td>
<td>100</td>
<td>17</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>Mid-Atlantic highlands</td>
<td>41</td>
<td>10</td>
<td>100</td>
<td>17</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>Forested lakes†</td>
<td>1640</td>
<td>14</td>
<td>100</td>
<td>17</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>Forested streams‡</td>
<td>1100</td>
<td>13</td>
<td>100</td>
<td>17</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>Atlantic Coastal Plain Lakes</td>
<td>20</td>
<td>11</td>
<td>100</td>
<td>17</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>Streams</td>
<td>1100</td>
<td>13</td>
<td>100</td>
<td>17</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>N. Florida highlands$</td>
<td>327</td>
<td>63</td>
<td>80</td>
<td>20</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>Streams</td>
<td>185</td>
<td>28</td>
<td>75</td>
<td>25</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>E. Upper Midwest</td>
<td>200</td>
<td>16</td>
<td>82</td>
<td>14</td>
<td>32</td>
<td>46</td>
</tr>
<tr>
<td>Low-silica lakes$</td>
<td>2311</td>
<td>1</td>
<td>2,311</td>
<td>14</td>
<td>32</td>
<td>46</td>
</tr>
</tbody>
</table>

*The southwest was defined as the part of the Adirondack physiographic province that receives >110 cm/yr precipitation. This is about one-third of the NSWS Adirondack lake population.
†About half the total population of streams and one-third of the lakes were in predominantly forested watersheds.
‡This includes about one-fourth of the lakes and half the streams in the Florida NSWS.
§We used silica as an indicator of ground-water contribution to low-silica lakes, defined as those with <1 mg/liter SiO$_2$.$\text{aq}$, about 43% of the NSWS lake population in the eastern Upper Midwest.

Finally, Krug and Frink (26) proposed that many clear-water, high-sulfate, acidic lakes were always acidic and that the major change resulting from acidic deposition has been the replacement (anion substitution) of organic anions with sulfate. Analysis of current chemistry cannot determine whether this process is important. Paleolimnological studies in the Adirondacks indicate, however, that inferred DOC concentrations have not declined substantially in acidic lakes (5, 18). Other lines of evidence suggest that this process is significant mainly in waters with rather high initial DOC concentrations (32).

We have identified populations of surface waters likely to have become chronically acidic as a result of acidic deposition. We emphasize that the population of chronically acidic NSWS surface waters is not the same as the population of surface waters whose biota have been impaired by acidic deposition. Acidic waters (2) usually have pH values less than 5.0 to 5.5, whereas biological effects can appear when pH declines below 6.0 or even 6.5 (24, 33). On the other hand, aluminum concentrations in acidic lakes in the Upper Midwest and Florida were lower than in lakes with comparable pH in the east, and some sport fishes (yellow perch, largemouth bass) in these lakes are relatively acid-tolerant. We have not considered short-term episodic acidification that may occur during peak flow periods (30, 34) or chronically acidic lakes and streams not represented in the NSWS (35). Taken as a whole, these considerations suggest that the population of surface waters impacted by acidic deposition is considerably larger than the population of chronically acidic systems in the NSWS; but available information indicates that the geographic distribution of waters impaired by acidic deposition in the United States corresponds closely with the high-interest areas shown in Fig. 1 (36).

REFERENCES AND NOTES
2. Following common convention, we define acidic waters as those having an acid neutralizing capacity (ANC) < 0 μeq/liter, based on Gran titration.
3. Recent acidification is defined as a loss of ANC that has occurred since the onset of industrial emissions approximately 100 years ago.
5. Much of the paleolimnological analysis of lake acidification in the United States has been conducted as part of the Paleolimnological Investigation of Recent Lake Acidification (PIRLA) studies. The PIRLA-I included small groups of low-ANC lakes in the Adirondacks, New England, Florida, and the Upper Midwest [D. F. Charles and D. R. Whitehead, Hydrobiologia 143, 13 (1986)]. In PIRLA-II, cores from 37 statistically representative lakes were analyzed to quantify lake acidification in the Adirondacks [D. F. Charles and J. P. Smol, Verh. Int. Verein. Limnol. 24, 474 (1990)].
7. The NSWS included three parts: the Eastern Lake Survey [D. H. Landers, W. S. Overton, R. A. Linthurst, D. F. Brakke, Environ. Sci. Technol. 22, 128 (1988)]; the Western Lake Survey [J. M. Eilers, D. F. Brakke, D. H. Landers, P. E. Kellar, Verh. Int. Verein. Limnol. 23, 144 (1988)]; and the National Stream Survey [F. R. Kaufmann, A. T. Herlihy, M. E. Mitch, J. M. Messer, W. S. Overton, Water Qual. Res. J. 27, 611 (1991)]. Samples were collected from 2,311 lakes, representing a population of 28,300 lakes, and 500 streams, representing a population of 64,300 streams. Data that we present are population estimates. Sampling was conducted at a time of the year in which chemical conditions are relatively stable (fall mixing in lakes and spring baseflow in streams); thus, the data represent chronic conditions in contrast to snowmelt or rainstorm episodes, when waters are generally more acidic. Details of this analysis are in (8).
9. Concentrations of major anions are compared on an equivalent basis. Sea-salt-corrected sulfate concentration [SO$_4^{2-}$] was calculated from measured [SO$_4^{2-}$]$^\text{aq}$ by subtracting the marine contribution using a marine SO$_4^{2-}$: Cl$^-$ ratio of 0.103. Because some waters were impacted by road salt, marine chloride contributions were calculated from a statistic driven distance-decay equation. We used the model of B. G. Oliver, E. M. Thurman, and R. L. Malcolm [Geochim. Cosmochim. Acta 47, 2031 (1983)] to calculate organic anion concentrations [(A$^-$)] from measured dissolved organic carbon (DOC) and pH. Two methods of calculating [(A$^-$)] were also examined: the anion-deficit approach and a regionalized calibration of the Oliver model for lakes [C. T. Driscoll, R. D. Fuller, W. D. Schecher, Water Air Soil Pollut. 43, 21 (1989)]. Classification by these alternative methods resulted in slightly lower percentages of organic-dominated waters (2).
10. This classification step was surprisingly robust. For example, no acidic streams changed categories when the classification criterion was changed from greater than 2 times the expected [SO$_4^{2-}$]$^\text{aq}$ to greater than 1.5 times the expected [SO$_4^{2-}$]$^\text{aq}$. Furthermore, all deposition-dominated acidic streams had [SO$_4^{2-}$]$^\text{aq}$ less than 250 μeq/liter, whereas all watershed sulfate-dominated acidic streams had [SO$_4^{2-}$]$^\text{aq}$ greater than 450 μeq/liter.
11. In examining SO$_4$:C$_n$ ratios, values of [C$_n$] were adjusted for sea and road salt influence by the assumption that cations from these sources are equivalent to measured [Cl$^-$]. Sea-salt-corrected C$_n$ values were labeled (C$_n$ – C$^\text{S}$).
13. Most acidic, high-DOC lakes that have been included in paleolimnological studies exhibit little recent acidification, although there are exceptions (Saugs Lake in Florida; Doe Lake in the Adirondacks) (5). High-DOC waters may be relatively resistant to acidification compared to low-DOC waters with comparable C$_n$–C$^\text{S}$ ratios. In the organic acid system [D. C. L. Lam, A. G. Bossa, R. A. Bourbonnãtre, G. D. Howell, M. E. Thompson, Water Air Soil Pollut. 46, 237 (1989)]. Whatever the source, there is a significant mineral acid component in many acidic, organic-dominated NSWS systems: for about 40% of the streams and 60% of the lakes in this category, [SO$_4^{2-}$ + NO$_3^-$] is greater than 50% of [C$_n$]. Acidification of some high-DOC waters as a result of industrial emissions cannot be ruled out.
14. About 80% of the organic-dominated acidic lakes had mapped wetlands in their watersheds. In contrast, 70% of the deposition-dominated acidic lakes had no mapped wetlands in their watersheds (8).
16. In the eastern United States, lakes with apparent
wastewater sources of sulfate are found primarily in watersheds with agricultural or urban land distur-
banes with higher pH and ANC than do lakes in the general NSWS population (8).


19. As of 1989, 14 New England lakes have been included in paleolimnological studies. Although this group is biased toward smaller, high-D0C lakes that are more likely to be acidic, 6 have undergone significant pH declines; only 1 showed a significant increase in pH [D. F. Charles, R. W. Bartolomucci, D. P. Dam, J. F. Sorensen, in Soils, Aquatic Processes, and Lake Acidification, vol. 4 of Acidity Precipitation, S. A. Norton, S. E. Lindberg, A. L. Page, Eds. (Springer-Verlag, New York, University of Florida, Gainesville, 1981).

20. Hydrologic budgets for about a dozen seepage lakes (mostly in northern Wisconsin) show that C4 con-
centrations in (5) are linearly related to ground-water inputs. Acidic seepage lakes in the Upper Midwest generally receive less than 10% of their water input from ground water; the rest is from precipitation to the lake surface [L. A. Baker, J. M. Eilers, R. B. Cook, P. R. Kaufmann, A. T. Herlihy, in Acidity Deposition and Aquatic Ecosystems: Regional Case Studies, D. F. Charles, Ed. (Springer-Verlag, New York, 1991), chap. 17]. Some Florida lakes also have low ground-water input [L. A. Baker, P. L. Breton, E. S. Edgerton, Water Resour. Bull. 22, 715 (1986)], but an ongoing study suggests that ground-water areas in some Florida is so depau-
erate of base cations that lakes with large ground-water inputs might also be sensitive to acidification (C. D. Pollman et al., in preparation).


22. We use the term "northern Florida highlands" to include the entire region (north of 29°N) of the Central Lake District and the Panhandle Districts [H. K. Brooks, Physiographic Divisions of Florida (Center for Environmental and Natural Resources, University of Florida, Gainesville, 1981)].

23. P. R. Sweets, R. W. Bierier, T. L. Crisman, M. W. Breton, J. Paleolimnol. 4, 103 (1990); additional ref.


28. E. C. Krog, P. J. Isaacson, and C. R. Frink [J. Air Pollut. Control Assoc. 35, 109 (1985)] argued that chronic acidic conditions in coastal areas may be caused by this mechanism, in which H+ is produced by retention of base cations caused by cation ex-
change, and a diamagnetic shielding of 7 percent could be obtained.

29. From the latter studies, Hebard et al. (6) have provided unambiguous evidence for superconductivity in solids composed of metallic Co60 molecules “doped” with po-
tassium (KCo60) with an onset near Tc = 18 K. They combined three experiments on two different morphologies (microwave ab-
sorption and magnetic susceptibility χ of powders, and dc resistivity of films) to assert superconductivity under unusually difficult, poorly controlled chemical conditions. As the powder is prepared by a solid-state reaction, only the initial composition is known, so no claim could be made about the homogeneity of the end product. Therefore, the actual composition of the superconduct-
ing phase was not directly determined, and the lower bound of 1% superconducting phase, established by shielding diamagnetism measurements, leaves open questions about the compositional stability of this phase within the K-Co60 phase diagram.

We report measurements of the shielding diamagnetism curves (χ versus T) conduct-
ed over a range of compositions and treat-
ments with the aim of separating and identi-
fying the superconducting phase. In an attempt to narrow the composition range of the superconducting material, the initial composition was systematically varied to locate the maximum fraction of shielding diamagnetism, which is a measure of the actual quantity of superconducting material. This maximum, found at a composition KCo60 ≈ 0.04%, a high value for a powder sample. This phase appears to be stable, that is, it is present after indefinitely long heating and mixing, for all nominal sample compo-
sitions, x < 0.5. When this same procedure

The recent report of a superconductivity onset near the critical temperature Tc = 18 K in potassium-doped Co60 raises questions concerning the composition and stability of the superconducting phase. The effects of mixing and heat treatment of KxCo60 samples prepared over a wide range of initial compositions on the superconducting transition was determined from shielding diamagnetism measurements. A single superconducting-
ting phase (Tc = 19.3 K) occurs for which the composition is KxCo60. The shielding reaches a maximum of greater than 40 percent of the perfect diamagnetism, a high value for a powder sample, in samples prepared from 3:1 mixtures. A RbCo60 sample prepared and analyzed in an analogous way exhibited evidence for superconductivity with Tc = 30 K and a diamagnetic shielding of 7 percent could be obtained.

T

HE RECENT DISCOVERY (1) and separation (2, 3) of molecular forms of solid carbon has made possible the formation of new semiconducting (4) and conducting (5) anionic charge-transfer compounds of Co60 (and C60) with molecular and alkali metal derivatives, respectively. From the latter studies, Hebard et al. (6) have provided unambiguous evidence for superconductivity in solids composed of metalated C60 molecules “doped” with po-
tassium (KCo60) with an onset near Tc = 18 K. They combined three experiments on two different morphologies (microwave ab-
sorption and magnetic susceptibility χ of powders, and dc resistivity of films) to assert superconductivity under unusually difficult, poorly controlled chemical conditions. As the powder is prepared by a solid-state reaction, only the initial composition is known, so no claim could be made about the homogeneity of the end product. Therefore, the actual composition of the superconducting phase was not directly determined, and the lower bound of 1% superconducting phase, established by shielding diamagnetism measurements, leaves open questions about the compositional stability of this phase within the K-Co60 phase diagram.

We report measurements of the shielding diamagnetism curves (χ versus T) conducted over a range of compositions and treatments with the aim of separating and identifying the superconducting phase. In an attempt to narrow the composition range of the superconducting material, the initial composition was systematically varied to locate the maximum fraction of shielding diamagnetism, which is a measure of the actual quantity of superconducting material. This maximum, found at a composition KCo60 ≈ 0.04%, a high value for a powder sample. This phase appears to be stable, that is, it is present after indefinitely long heating and mixing, for all nominal sample compositions, x < 0.5. When this same procedure

Akali-Fulleride Superconductors: Synthesis, Composition, and Diamagnetic Shielding

KÁROLY HOLCZER, OLIVÉR KLEIN, SHIYOU-MEI HUANG, RICHARD B. KANER, KE-JIAN FU, ROBERT L. WHETTEN, FRANÇOIS DIEREDIER

The recent report of a superconductivity onset near the critical temperature Tc = 18 K in potassium-doped Co60 raises questions concerning the composition and stability of the superconducting phase. The effects of mixing and heat treatment of KxCo60 samples prepared over a wide range of initial compositions on the superconducting transition was determined from shielding diamagnetism measurements. A single superconducting phase (Tc = 19.3 K) occurs for which the composition is KxCo60. The shielding reaches a maximum of greater than 40 percent of the perfect diamagnetism, a high value for a powder sample, in samples prepared from 3:1 mixtures. A RbCo60 sample prepared and analyzed in an analogous way exhibited evidence for superconductivity with Tc = 30 K and a diamagnetic shielding of 7 percent could be obtained.

THE RECENT DISCOVERY (1) and separation (2, 3) of molecular forms of solid carbon has made possible the formation of new semiconducting (4) and conducting (5) anionic charge-transfer compounds of Co60 (and C60) with molecular and alkali metal derivatives, respectively. From the latter studies, Hebard et al. (6) have provided unambiguous evidence for superconductivity in solids composed of metalated C60 molecules “doped” with potassium (KCo60) with an onset near Tc = 18 K. They combined three experiments on two different morphologies (microwave absorption and magnetic susceptibility χ of powders, and dc resistivity of films) to assert superconductivity under unusually difficult, poorly controlled chemical conditions. As the powder is prepared by a solid-state reaction, only the initial composition is known, so no claim could be made about the homogeneity of the end product. Therefore, the actual composition of the superconducting phase was not directly determined, and the lower bound of 1% superconducting phase, established by shielding diamagnetism measurements, leaves open questions about the compositional stability of this phase within the K-Co60 phase diagram.

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