Large thermopower in NaCoO₄:
a novel physical property in transition-metal oxides

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The discovery of high-temperature superconductivity in copper oxides has made two great impacts on basic science. The one is to deny the superstition that only a mega-science like particle experiments can discover new physics. The other is to remove the wall between physics and chemistry: physicists have begun to synthesize many samples, and chemists have begun to measure physical properties very precisely.

I was a graduate student in Shoji Tanaka’s laboratory in the University of Tokyo, when high-temperature superconductivity was reported by Bednorz and Muller. My colleagues reexamined Bednorz and Muller’s experiment, and I was surprised to see that the superconductivity in copper oxides survived above 23 K! Since then, I have been involved with the study of high-temperature superconductivity.

I am interested in non-superconducting transition-metal oxides. I believe that, if I understand why they are non-superconductive, I can understand why the copper oxides show superconductivity. Since the superconducting copper oxides have the CuO₂ plane (the two-dimensional square lattice of antiferromagnetic spins) as a common unit, I thought a triangular lattice of antiferromagnetic spins as a good reference, and eventually have met with the Co oxide NaCoO₄.

NaCoO₄ is an old material which was synthesized and identified in 1970’s. This material is a layered oxide in which the CoO₂ block and the Na block alternately stack along the c direction. The CoO₂ block is responsible for electric conduction, where magnetic Co ions form a triangular lattice. We succeeded in making single crystals, and measured the resistivity and the thermopower (voltage induced by an applied temperature gradient) along the layer direction. The resistivity is as low as 200 µΩcm
at room temperature, which is nearly the same resistivity for high-temperature superconducting copper oxides. On the contrary, the thermopower is as large as 100 $\mu$V/K at room temperature, which is ten times larger than a typical thermopower of high-temperature superconducting copper oxides.

The large thermopower accompanied by the low resistivity indicates that NaCo$_2$O$_4$ behaves like a battery in a temperature gradient. Such a material is called a thermoelectric material. The thermoelectric material can convert heat into electric power through the Seebeck effect, and electric power into heat through the Peltier effect. It can generate electricity from waste heat, and can refrigerate foods and drinks without a Freon-gas compressor. Although most of oxides were poor thermoelectric materials, NaCo$_2$O$_4$ is exceptionally good, whose thermoelectric parameters are comparable to (or even better than) those of the conventional thermoelectric materials (Bi$_2$Te$_3$, PbTe).

NaCo$_2$O$_4$ is not a simple new thermoelectric material. The conventional thermoelectric materials are semiconductors with a carrier concentration of $10^{19}$ cm$^{-3}$, but NaCo$_2$O$_4$ has the carrier concentration of $10^{21}$ to $10^{22}$ cm$^{-3}$, which is verified by the Hall coefficient measurement. This is a typical carrier for a metal, and is 100-1000 times larger than that for the conventional thermoelectric materials. Thus the problem is how the metallic carrier concentration causes a large thermopower of the order of 100 $\mu$V/K.

Another fascination of NaCo$_2$O$_4$ is existence of various related oxides. Following NaCo$_2$O$_4$, Ca$_3$Co$_4$O$_9$, (Bi,Pb)$_2$Sr$_2$Co$_2$O$_8$, TlSr$_2$Co$_2$O$_y$, and (Hg,Pb)Sr$_2$Co$_2$O$_y$ have been found to show good thermoelectric performance. The triangular CoO$_2$ block is common to these cobalt oxides, which reminds us of the CuO$_2$ plane in high temperature superconductors. Thus, just as the CuO$_2$ plane, the triangular CoO$_2$ block should be a key ingredient for the unusually high thermoelectric performance of the layered cobalt oxides.

The microscopic theory for the high thermoelectric performance of NaCo$_2$O$_4$ is still lacking, but we think that the following features are now established.

1. The mixture of Co$^{3+}$ and Co$^{4+}$ in the low spin state can carry large entropy of $k_B \log 6$, which gives a large thermopower of $k_B \log 6/e=150 \mu$V/K in the high-temperature limit.
(2) NaCo$_2$O$_4$ shows no structural, electric, and magnetic transitions from 2 to 1000 K. 
(3) From (1) and (2), the large entropy cannot be released through phase transitions, and inevitably point to the conducting carriers to form a “heavy-fermion”-like state. In fact, the thermodynamic properties of NaCo$_2$O$_4$ are very similar to those of heavy-fermion compounds. Recently, a coherent state like a Kondo resonance (a hallmark of a heavy fermion) is observed in the photoemission spectra of NaCo$_2$O$_4$ at low temperatures.

I would like to emphasize that the heavy-fermion-like state in NaCo$_2$O$_4$ should be microscopically unique, because it is realized after all the phase transitions are suppressed or blocked. Thus I hope that the microscopic understanding of this material will give new physics in condensed matter.

Another example for the reference material is the one-dimensional copper oxide CuGeO$_3$. This material has the chain structure of Cu$^{2+}$ instead of the plane structure of Cu$^{2+}$ in high-temperature superconductors. We tried to dope carriers in this compound, but failed to make conducting samples. Instead, however, we found that this material shows an unexpected phenomenon, the spin-Peierls transition. The spin-Peierls transition is a transition that a uniform antiferromagnetic spin-$1/2$ chain changes to a dimerized chain below a transition temperature via the spin-phonon interaction. Since the dimerized spin pair forms a spin-singlet, the ground state is nonmagnetic with a finite energy gap in the spin excitation. At present, CuGeO$_3$ is the only inorganic compound exhibiting the spin-Peierls transition.

These two discoveries share common features. (1) Synthetic method and crystal structure of the two materials were reported much before by chemists. In this sense, these are not new materials. (2) Basic quantities (thermopower of NaCo$_2$O$_4$ and magnetic susceptibility of CuGeO$_3$) were also measured by chemists. (3) We found the two new functions by precise measurements with high-quality crystals, but our initial motivation was far away from the findings.

It seems to include a hint of material search for a physicist. It is to search for a function, not for a material. It is to draw an unexpected function from the material by precise measurement. Such a function would not be found at all in a carpet-bombing-style search like combinatorial chemistry, because the measurer himself does not know what to find. Thereupon, we can find an advantage for a physicist carrying out the material search.