Letters to the Editor

Ferroelectricity in the Alums*

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GRANIER[1] has reported peaks in the curve of the dielectric constant *versus* temperature in ammonium iron alum (−180°C) and ammonium aluminum alum (−220°C). Extensive evidence of electronic transitions in these and other alums is available from paramagnetic resonance measurements; these results have recently been summarized by Bowers and Owen.[2] In a reinvestigation of the optical, dielectric, and structural properties of a large number of alums, we have discovered ferroelectric behavior in a number of these, and antiferroelectricity in others.

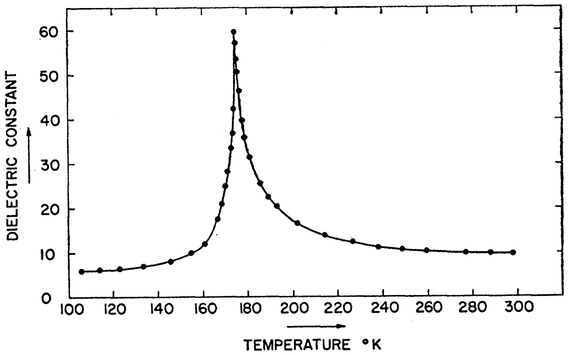


FIG. 1. Methylammonium aluminum alum, $(\mathrm{NH_3CH_3})\mathrm{Al(SO_4)_2}\cdot 12\mathrm{H_2O}$: dielectric constant, measured along the cubic [111] direction, as a function of absolute temperature.

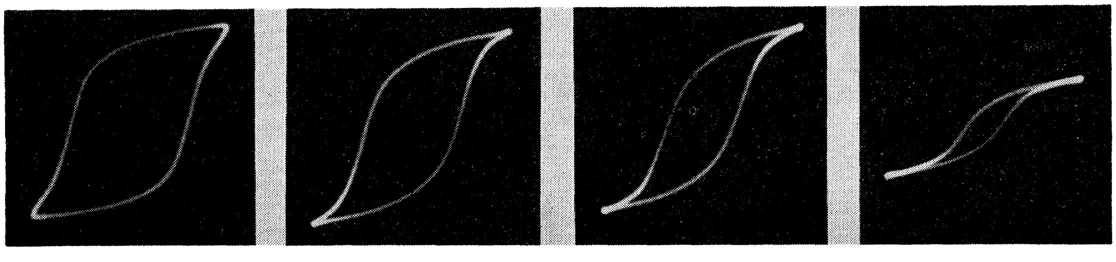
The behavior of $(\mathrm{CH_3NH_3})\mathrm{Al(SO_4)_2}\cdot 12\mathrm{H_2O}$, methylammonium aluminum sulfate dodecahydrate (abbreviated MASD), is typical of the ferroelectric compounds. Figure 1 shows the curve of the dielectric constant ϵ, observed along the cubic [111] direction, as a function of temperature. The room-temperature value of ϵ is about 9; and it reaches a peak of about 60 at the Curie point, at about 176°K. A plot of $1/\epsilon$ *versus* temperature reveals adherence to a Curie-Weiss law in a rather narrow temperature range ($\approx 25°$) above the Curie point. The Curie constant C is about 1000°. The dielectric peak is accompanied by a very sharp peak in the loss factor. At and just below the Curie point, characteristic hysteresis loops of polarization *versus* field are observed, as shown in Fig. 2 for four different temperatures.

A striking property of these ferroelectrics is that the coercive field E_c is unusually large, and increases rapidly with decreasing temperature. E_c is of the order of magnitude of 5 kv/cm within two degrees below the Curie point, and rises to 15 kv/cm about 25° below the transition, for MASD. Saturated ferroelectric loops can consequently be observed only in a narrow range below the Curie point (about 20°). The value of the spontaneous polarization P_s of MASD at 166°K is approximately 0.6 microcoulomb/cm²—which is 2 or 3 times higher than that for Rochelle salt at 0°C.

Urea chromium alum has a Curie point at 160°K, and a P_s value of approximately 0.1 microcoulomb/cm².

We have prepared a large number of substituted-ammonium alums, most of which show crystal transitions above liquid nitrogen temperature. We have also examined a large number of alums with K or $\mathrm{NH_4}$ as monovalent and Al, Cr, Fe, Ce, and In as trivalent ions; and we have investigated the effects of deuteration, and of substitution of $\mathrm{SeO_4}$ and $\mathrm{S_2O_3}$ for $\mathrm{SO_4}$ ions. Some of these crystals have transition points below 77°K, and some indicate antiferroelectric behavior. Details of these and other observations will be reported subsequently.

It is interesting that we have been able to prepare guanidinium aluminum sulfate and the corresponding chromium salt as alums. Guanidinium aluminum alum has a transition immediately above liquid nitrogen temperature. Normal preparation of the guanidinium



154°K 163°K 171°K 177°K

FIG. 2. Hysteresis loops of methylammonium aluminum alum, $(\mathrm{NH_3CH_3})\mathrm{Al(SO_4)_2}\cdot 12\mathrm{H_2O}$, at four different temperatures.

salts leads to the hexagonal hexahydrates, the ferroelectric behavior of which has been reported by Holden, Matthias, Merz, and Remeika.[3]

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[1] J. Granier, *Les Diélectriques* (Dunod, Paris, 1948).

[2] K. D. Bowers and J. Owen, Repts. Progr. in Phys. **18**, 305 (1955).

[3] Holden, Matthias, Merz, and Remeika, Phys. Rev. **98**, 546 (1955).

Resistivity Increase in Water-Quenched Gold*

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Upon quenching into water from a high temperature (650–950°C) an increase in the resistivity of gold wires (99.999% pure, 16 and 30 mil diameter) has been observed. The increase is describable by an equation of the form $\Delta\rho = Ae^{-E_F/kT}$, where $\Delta\rho$ is the increase in resistivity, A is a constant, T is the absolute temperature from which the quench is made, and E_F is the energy of formation of the defects responsible for the resistivity increase. It is found that $E_F = (1.02 \pm 0.06)$ ev, and that for a quench from 800°C, $\Delta\rho = 1.2 \times 10^{-8}$ ohm-cm. Sample results are shown in Fig. 1. All measurements were made at liquid-nitrogen temperature. The total time required to quench to room temperature ranged from 20 to 50 milliseconds. If too slow a quench is used, deviations occur at the higher temperatures as shown by the points marked × for specimen number 6. Experiments using other liquid quenching media indicate that the results are independent of the liquid used.

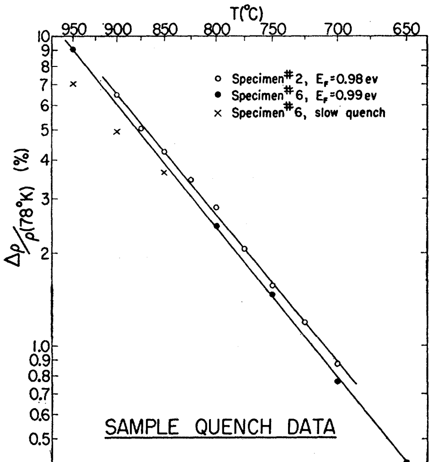

Fig. 1. The dependence of the quenched-in resistivity on the quenching temperature. Note that slow quenches indicated by × give points falling below the expected exponential dependence, particularly at high temperatures.

At least 90% of the quenched-in resistance anneals out at room temperature, and isothermal annealing measurements yield an energy of motion of (0.66±0.06) ev for the defects. This agrees with the previous work of Kauffman and Koehler,[1] who reported a value of $E_M = (0.68 \pm 0.03)$ ev. The initial part of the annealing curve deviates somewhat from that for a second-order process. For a quench from 800°C with no deformation present, approximately 70 hours are required for half of the quenched-in resistance to anneal out at 30°C. Quenches involving small amounts of deformation from below 950°C give the same value of $\Delta\rho/\rho$ as those in which no deformation occurred. The rate of annealing and the energy of motion were, however, strongly affected by deformation. The rate increased on deformation by at least an order of magnitude and the apparent energy of motion was decreased in some cases to less than half the value found when deformation is not present. The annealing behavior was used as a sensitive test for any deformation which might occur during the quench.

Assuming that the defects involved are vacancies, the activation energy for self-diffusion in gold is found to be $Q = E_F + E_M = (1.68 \pm 0.12)$ ev, which compares favorably with $Q = 1.70$ ev found by Okkerse[2] using tracer techniques.

Further measurements on gold, and also on silver and copper are in progress.

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Mass of B^{13} from the Nuclear Reaction $Li^7(Li^7,p)B^{13}$

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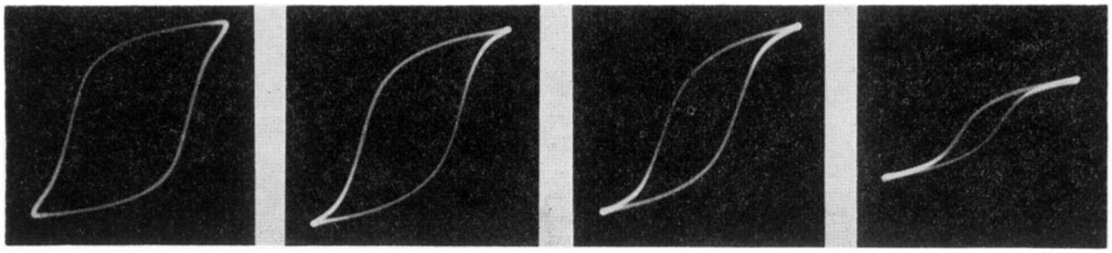
It has been predicted that the nuclear species ${}_5B^{13}$ will be found to be stable with respect to disintegration into heavy charged particles,[1] and Snell[2] has suggested that it may, by analogy with N^{17}, be a delayed-neutron emitter. The delayed neutrons have been searched for in fission and spallation fragments with negative results.[3,4] We have found that B^{13} may be prepared by means of the reaction $Li^7(Li^7,p)B^{13}$.

A 2-Mev Van de Graaff accelerator has been converted to the acceleration of Li ions, obtained by



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