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Physical Properties of Chromium Alums at Low Temperatures

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INTRODUCTION

THE physical properties of chromium alums have been extensively studied by both experimental and theoretical physicists. These alums are of interest primarily because they are paramagnetic. Although they are far from unique in this respect, attention has been focused on them by experimenters because they are inexpensive and can easily be prepared in the form of large single crystals. Apart from their intrinsic interest they are studied because they are frequently used in adiabatic demagnetization experiments as coolants and as thermometers. The interest of theoretical physicists in the chromium alums is enhanced by the availability of considerable experimental data. These data have been taken at temperatures from about 25°C to a few millidegrees absolute in static magnetic fields of strengths up to 60,000 oersteds and in alternating fields of frequencies up to 25,000 megacycles per second. Nevertheless, the available information is far from complete and is only imperfectly understood from a theoretical point of view.

The chemical formula for the alums which will be discussed here is $X\mathrm{Cr(SO_4)_2 \cdot 12\ H_2O}$ where X denotes the monovalent cation. Experiments have been performed with potassium, cesium, rubidium, thallium, ammonium, methylamine, and hydroxylamine ions as cations. Attempts to grow sodium chromium alum crystals have been unsuccessful. Many of the corresponding selenate alums (including sodium chromium selenate alum) are known but their magnetic properties have not been studied.

I. CRYSTAL STRUCTURE

The crystal structure of the similar aluminum sulfate alums was determined by Lipson and Beevers[1] by x-ray methods. The lattice is simple cubic with aluminum (or chromium) ions at alternate corners of a unit cube. Each of the trivalent anions is surrounded by six water molecules in a nearly octahedral arrangement, the axes of the octahedron nearly coinciding with those of the lattice. It is believed that each octahedron of water molecules is slightly distorted along a trigonal axis of the unit cell.[2]

Subsequent study of the aluminum alums by Lipson[3] revealed a structural polymorphism. There are at least three slightly different structures which Lipson called α, β, and γ. The structures are characterized by the positions of the sulfate ions along trigonal axes of the unit cell. The division into groups depends, roughly, on the size of the monovalent cation. Lipson's α-type includes K, $\mathrm{NH_4}$, Tl, and Rb aluminum alum; his β-type includes Cs and $\mathrm{NH_3CH_3}$ aluminum alum. The only cation in the γ-structure group is Na.

X-ray determinations of the structure of the chromium sulfate alums were made by Klug.[4] He found that only K and $\mathrm{NH_4}$ chromium alum crystallize with the α-type structure. Rb, Cs, Tl, and $\mathrm{NH_3CH_3}$ chromium alum have the β-type structure. It is evident from the fact that the structures of the Rb and Tl chromium and aluminum alums are different that one must exercise discretion when diluting a paramagnetic salt by replacing the magnetic anion by a nonmagnetic ion.

II. STRUCTURAL TRANSITIONS

In 1939 Guillien[5] discovered that in KCr alum, $\mathrm{NH_4Cr}$ alum, and other alums at about 85°K there is a sudden decrease in the dielectric constant. In the course of optical absorption spectra studies of chromium alums, Kraus and Nutting[6] found a transition in $\mathrm{NH_4Cr}$ alum at 81°K that disrupted the lattice. Microwave resonance absorption experiments by Bleaney and Penrose[7,8] and by Kip *et al.*[9] have also revealed the existence of a transition in K and $\mathrm{NH_4Cr}$ alums (although it is of somewhat different character in the two salts) but not in the other chromium alums. Apparently the transition occurs only in those which have the α-type structure. It should therefore be expected to occur in KCr alum or $\mathrm{NH_4Cr}$ alum when magnetically diluted with the corresponding aluminum alums.

According to Kraus and Nutting, on cooling through the transition temperature the crystals of $\mathrm{NH_4Cr}$ alum suddenly become opaque and seem to have shattered. On warming the crystals regain their transparency. Both the optical and the microwave measurements

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[1] H. Lipson and C. A. Beevers, Proc. Roy. Soc. (London) **A148**, 664 (1935).

[2] This idea is due to J. H. Van Vleck, J. Chem. Phys. **7**, 61 (1939).

[3] H. Lipson, Proc. Roy. Soc. (London) **A151**, 347 (1935).

[4] H. P. Klug, J. Am. Chem. Soc. **62**, 2992 (1940).

[5] R. Guillien, Compt. rend. **209**, 21 (1939).

[6] D. L. Kraus and G. C. Nutting, J. Chem. Phys. **9**, 133 (1941). Kraus and Nutting divided the alums they studied into three types, the division being based on similarity of spectra. The classification does not completely agree with Klug's.

[7] B. Bleaney and R. P. Penrose, Proc. Phys. Soc. (London) **60**, 395 (1948).

[8] B. Bleaney, Phys. Rev. **75**, 1962 (1949).

[9] A. F. Kip *et al.*, (to be published). I wish to thank Professor Kip for making his data available to me prior to publication.

reveal temperature hysteresis effects. It is probable that a structural transition takes place which involves the water-containing complexes.[6,10] The strains induced in the NH_4Cr alum lattice when it is cooled are relieved by shattering of the crystal. A more gradual transition takes place in KCr alum. In the modified lattice which is stable at the lower temperatures the chromium ions are acted on by electric fields of slightly altered strength and symmetry. The structural transition is probably of great importance for the low temperature behavior. It would be extremely useful to have an x-ray determination of the structure in the temperature region below the transition point.

III. SUSCEPTIBILITY

The susceptibility of KCr alum has been measured down to 14°K by de Haas and Gorter,[11] and by Gorter, de Haas, and van den Handel[12] between 4.27 and 1.34°K. As nearly as one can tell from the published curves, there is no change of slope of the χ *versus* T curve at the transition temperature. This result is to be expected since the orbital angular momentum is almost completely quenched by the crystalline fields both above and below the transition point. The susceptibility should, therefore, be given by the so-called "spin-only" formula. A better approximation to the measurements is the Curie-Weiss law $\chi=C(T-\Delta)^{\frac{1}{2}}$ with $\Delta=0.16°$. Gorter, de Haas, and van den Handel also studied the effects of beginning saturation on the susceptibility. Recent measurements by Henry[12a] extend up to 99.5 percent saturation.

Measurements of the alternating current susceptibility will be discussed in Sec. VI and measurements below 1°K in Sec. IX.

IV. THERMAL CONDUCTIVITY

Thermal conductivity measurements have been made on KCr alum by Bijl[13] and by Garrett.[14] Bijl found in experiments on an imperfect single crystal that the thermal conductivity between approximately 1° and 4°K depends on the rate at which the crystal is cooled from 70°K to liquid helium temperatures. The conductivity in the liquid helium region is about 0.1-watt cm^{-1} deg^{-1} although it varies considerably with temperature. It seems possible that the differing conductivities could be due, at least in part, to the treatment of the sample near the transition temperature which may be quite variable. Kraus and Nutting[6] were sometimes able to keep NH_4Cr alum in an unshattered condition in liquid hydrogen. At any rate, the fact that the thermal conductivity depends on the rate of cooling suggests that the quality referred to by various authors as "physical purity" depends on the thermal history of the sample.

Garrett's measurements were made on a long single crystal of KCr alum at temperatures between 0.14 and 0.30°K. He found that K/T^3 is approximately 5.3×10^5 ergs sec^{-1} cm^{-1} deg^{-4}. Here K is the thermal conductivity. Garrett's curve of K *versus* T, when extrapolated, agrees with Bijl's results for the sample which was cooled slowly.

It would be interesting if thermal conductivity measurements were available on a nonmagnetic alum, as Bijl suggests. It would also be interesting, and probably more feasible from an experimental standpoint, to make measurements on a chromium alum with the β-structure.

V. MICROWAVE RESONANCE ABSORPTION

Microwave resonance absorption spectra have been obtained by numerous investigators.[7–10,15–18] The room temperature spectra for all the chromium alums are more or less the same and can be accounted for nicely by the theory set forth by Broer[19] or by Weiss.[16] The ground state of the free Cr^{+++} ion is ^4F. In the crystalline field of the lattice which has predominantly cubic symmetry the orbital degeneracy is partially removed. The lowest state of the Cr^{+++} ion in the lattice is orbitally nondegenerate and is separated from the higher orbital triplets by about 10,000 cm^{-1} and 18,000 cm^{-1}. Because of the quenching of the orbital angular momentum by the crystalline field the lowest state is effectively ^4S. The fourfold spin degeneracy of this state is partially lifted by the combined action of a small crystalline field of trigonal symmetry and the spin-orbit interaction. Two close-lying doublets remain separated by 0.3 cm^{-1} or less. This splitting is proportional to the magnitude of the trigonal field and, therefore, is a measure of the distortion of the octahedron of water molecules which surrounds each Cr^{+++} ion. It can easily be determined from the microwave absorption spectra. The splitting does not depend very sensitively on temperature in alums of the β-type. However, in KCr and NH_4Cr alum the splitting decreases with decreasing temperature and is nearly zero at the transition point. The change of splitting is presumably associated with rotation of the water molecules. At lower temperatures there are apparently two or three different splittings in the same salt which are nearly temperature independent. This fact can only be explained by assuming that not every chromium ion is in the same electrostatic environment.[20]

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[10] Kip, Malvano, and Davis, Phys. Rev. **82**, 342A (1951).

[11] W. J. de Haas and C. J. Gorter, Proc. Koninkl. Nederland Acad. Wetenschap. **33**, 676 (1930), Leid. Comm. No. 208c.

[12] Gorter, de Haas, and van den Handel, Proc. Koninkl. Nederland Acad. Wentenschapp. **36**, 158 (1933). Leid. Comm. No. 222d.

[12a] W. E. Henry, Phys. Rev. **85**, 487L (1952).

[13] D. Bijl, Physica **14**, 684 (1949).

[14] C. G. B. Garrett, Phil. Mag. **41**, 621 (1950).

[15] Cummerow, Halliday, and Moore, Phys. Rev. **72**, 1233 (1947).

[16] P. R. Weiss, Phys. Rev. **73**, 470 (1948).

[17] R. Malvano and M. Panetti, Nuovo cimento **7**, 28 (1950).

[18] B. Bleaney, Proc. Roy. Soc. **A204**, 203 (1950). This list of papers on microwave absorption in chromium alums is not complete.

[19] L. J. F. Broer, Physica **9**, 547 (1942).

[20] J. Eisenstein, Phys. Rev. **82**, 342A (1951).

VI. PARAMAGNETIC RELAXATION

Much work has been done on the alternating current susceptibility of KCr alum and NH_4Cr alum.[21–25] Measurements have been made at temperatures down to about 0.0015°K, at frequencies up to approximately 100 Mc, and in constant fields of strengths up to 60,000 oersteds oriented both parallel and perpendicular to the oscillatory magnetic field. These ac measurements are usually referred to by the name "paramagnetic relaxation."[26] It is customary to distinguish between two relaxation phenomena, known as spin-spin and spin-lattice relaxation.[27] In the former, the relaxation time involved is the time required for the system of all ionic spins to come to equilibrium in an applied magnetic field. In the latter the relaxation time is essentially the time required for the transfer of the heat of magnetization from the spin system to the lattice. The two relaxation phenomena can be studied separately since the spin-lattice relaxation time is of the order of 10^{-7} sec at liquid air temperatures and increases to 10^{-2} sec at liquid helium temperatures, while the spin-spin relaxation time is of the order of 10^{-9} sec and is independent of temperature.

Casimir and du Pré[28] developed a phenomenological, thermodynamic theory which connects the spin-lattice relaxation time with the real and imaginary parts of the susceptibility and the specific heats of the salt. Their formulas are

$$\chi'=\chi_0F(1+\omega^2\tau^2)^{-1}+\chi_0(1-F), \tag{1}$$

$$\chi''=\chi_0F\omega\tau(1+\omega^2\tau^2)^{-1}, \tag{2}$$

$$F=(c_H-c_M)/c_H; \quad \tau=c_H/\alpha. \tag{3}$$

Here $\chi=\chi'-i\chi''$ is the measured susceptibility, χ_0 is the isothermal susceptibility, τ is the spin-lattice relaxation time, c_M and c_H are the specific heats of the spin system at constant magnetization and constant field, respectively, and α is a coefficient of thermal contact between the spin system and the lattice. These formulas should apply whenever τ is long compared with the spin-spin relaxation time.

The data can usually be satisfactorily fitted to these formulas; the agreement of experiment and theory seems too good to be entirely fortuitous. However, recent measurements of Kramers, Bijl, and Gorter[29] of Bijl,[30] and of Benzie and Cooke[31] at liquid helium temperatures on numerous paramagnetic salts do not agree with the Casimir-du Pré formulas. These experimenters have suggested that their results could be accounted for by assuming a distribution of relaxation times rather than a single one. Some years ago Kronig[32] predicted on theoretical grounds that more than one spin-lattice relaxation time might be involved in the attainment of equilibrium but the experimental results seem even more complicated than he envisioned. The writer[33] has generalized the Casimir-du Pré theory slightly by taking into account the thermal conductivity of the salt, but the modified theory is still inadequate to account for the experimental results. Since the approximation that the spin-lattice relaxation time is much longer than the spin-spin relaxation time should be particularly good at liquid helium temperatures, the domain of validity of the above formulas is in doubt.

Kramers, Bijl, and Gorter[29] have found that the physical and chemical purity of the specimen affect the relaxation time;[34] in particular, τ for KCr alum is altered by recrystallization. It is possible that the relaxation times depend on the thermal histories of the specimens and that shattering of the crystals when they pass through their transition temperatures is the factor chiefly responsible for the varying physical purity of the samples. Unfortunately for this explanation it seems unlikely that all the salts which show deviations from the Casimir-du Pré relations have structural transitions. Benzie and Cooke[31] state that these relations are not satisfied by measurements made on CsCr alum. More measurements on this alum or others of the β-type might, however, be interesting.

In the Casimir-du Pré theory α (or τ) appears as an empirical parameter. Van Vleck[35] calculated formulas for KCr alum on the basis of a microscopic, quantum-mechanical theory. The calculation is rather involved. The predicted dependence of τ on temperature is roughly correct and the relaxation times have about the right order of magnitude. However, the calculated dependence of τ on magnetic field strength at helium temperatures is completely wrong. It seems likely that the structure of KCr alum at low temperatures is very much more complicated than at room temperature. With experimental data lacking the formulation of an adequate microscopic theory is very difficult.

The spin-spin relaxation time is derived by assuming that the high frequency susceptibility satisfies a formula like (2) and that for the highest frequencies used experimentally ($\nu\sim10^2$ Mc) $\omega\tau\ll1$. It follows that the energy absorption per second, which is given by a constant times $\nu\chi''$, is proportional to ν^2. The constant

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[21] Gorter, Dijkstra, and Groendijk, Physica **7**, 625 (1940).

[22] Casimir, Bijl, and du Pré, Physica **8**, 449 (1941).

[23] Dijkstra, Gorter, and van Paemel, Physica **9**, 673 (1942).

[24] Volger, de Vrijer, and Gorter, Physica **13**, 635 (1947).

[25] C. Starr, Phys. Rev. **60**, 241 (1941). This list of papers on paramagnetic relaxation in chromium alums is not complete.

[26] See the book, *Paramagnetic Relaxation* by C. J. Gorter (Elsevier Publishing Company, Amsterdam, Holland, 1947). See also a review article by A. H. Cooke in Rep. Prog. Phys. **XIII**, 278 (1950).

[27] A third type of relaxation has been discovered by F. W. de Vrijer and C. J. Gorter, Physica **14**, 617 (1949).

[28] H. B. G. Casimir and F. K. du Pré, Physica **5**, 507 (1938).

[29] Kramers, Bijl, and Gorter, Physica **16**, 65 (1950).

[30] D. Bijl, Physica **16**, 269 (1950).

[31] R. J. Benzie and A. H. Cooke, Proc. Phys. Soc. (London) **A63**, 201 (1950).

[32] R. de L. Kronig, Physica **5**, 65 (1938).

[33] J. Eisenstein, Phys. Rev. **84**, 548 (1951).

[34] This same suggestion is made in reference 22.

[35] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

of proportionality is essentially the spin-spin relaxation time. Broer[36] has worked out a microscopic theory which yields spin-spin relaxation times in order of magnitude agreement with experiment. Calculations relating specifically to KCr alum have been made by Ishiguro, Kambe, and Usui.[37] By including a proper amount of exchange interaction they obtain a theoretical spin-spin relaxation time in zero magnetic field which is in rather good agreement with experiment.

VII. SPECIFIC HEAT

The specific heat can be determined calorimetrically or from susceptibility measurements or by a combination of the two methods in which heat is supplied by the relaxation losses and the rate of rise of temperature is observed.[38] The susceptibility method depends on the following relations which hold independently of any assumptions about the relaxation times:

$$\chi_0/\chi_s = c_H/c_M, \quad c_H - c_M = T(\partial M/\partial T)_H{}^2\chi_0^{-1}.$$

Here χ_s is the adiabatic or high frequency susceptibility and the other quantities have been defined previously. The specific heat can, in principle, be calculated from the partition function. The general problem of calculating the partition function has been considered by Van Vleck[39] and his results applied to various paramagnetic salts by Hebb and Purcell[40] and others. The principal difficulty lies in the evaluation of the effects of the interaction of neighboring magnetic ions.

Measurements of specific heat have been made on KCr alum by Kürti and Simon,[41] on NH_4Cr and CsCr alums by Benzie and Cooke,[42] and on KCr alum by Bleaney.[43] It has been customary in the past to deduce from specific heat or susceptibility data values of the doublet splitting of the ground state of the Cr^{+++} ion. The values varied somewhat but were approximately 0.18 cm^{-1} for KCr alum. As stated previously, it now appears that at low temperatures two or three splittings exist in KCr and NH_4Cr alum. Consequently, the energy level separations so calculated for these salts are without significance.

Microwave resonance experiments provide direct information about the ground-state splitting. If the number of Cr ions in KCr alum having each splitting were known, it would be possible to compute the specific heat. However, Bleaney has found that it is impossible to obtain agreement of theory and experiment no matter what one assumes about the number of ions with given splitting. According to Benzie and Cooke, the specific heat data on NH_4Cr alum can be reconciled with the known splittings. For CsCr alum the splittings calculated from specific heat and microwave absorption data are in good agreement.

VIII. MAGNETIC DILUTION

KCr alum and NH_4Cr alum can be magnetically diluted by replacing the Cr^{+++} ion by Al^{+++}. Since the corresponding aluminum alums also have the α-structure, it is probable that the mixed crystals have this structure. Various properties of the alums will be affected by dilution. The microwave absorption lines are narrowed[10] since the chief source of line breadth is the magnetic interaction of neighbors. In the very low temperature region the specific heat is due largely to the magnetic interaction and should be decreased.

Only a few experiments on magnetically dilute alums have been performed. Bijl[44] measured relaxation times at helium temperatures in a diluted specimen which contained 13 Al^{+++} ions to 1 Cr^{+++} ion. He found that the spin-lattice relaxation time is considerably longer in the dilute salt. This result is surprising since one expects τ to depend only on the interaction of the spins with the lattice vibrations via the spin-orbit and orbit-lattice couplings. The normal modes of the $Cr^{+++}\cdot 6\,H_2O$ cluster should be nearly independent of the chromium concentration. Bijl also found that at 1.21°K the relaxation time decreases with increasing H in contrast to its behavior in the undiluted salt, but in accordance with Van Vleck's theory. The general dependence of τ on dilution seems corroborated by recent experiments of Benzie[45] on other salts.

Diluted KCr alum has been used in adiabatic demagnetization experiments to reach extremely low temperatures. The present record for a single demagnetization of 0.0015°K was set by de Klerk, Steenland, and Gorter[46] who used a specimen containing 1 Cr ion to 20 Al ions. Darby and others[46a] used a diluted chromium alum in the second stage of a two stage adiabatic demagnetization apparatus. They estimate the lowest temperature reached was about 10^{-3} °K.

IX. ADIABATIC DEMAGNETIZATION AND TEMPERATURE MEASUREMENT

Potassium chromium alum has been used by numerous experimenters in the magnetic cooling method.[47–53] Its suitability *vis-à-vis* a β-type alum is, of course,

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[36] L. J. F. Broer, Physica **10**, 801 (1943).

[37] Ishiguro, Kambe, and Usui, Phys. Rev. **82**, 680 (1951).

[38] Casimir, de Haas, and de Klerk, Physica **6**, 255 (1939).

[39] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937).

[40] M. Hebb and E. Purcell, J. Chem. Phys. **5**, 338 (1937).

[41] N. Kürti and F. Simon. The measurements are cited in Reference 40.

[42] R. J. Benzie and A. H. Cooke, Proc. Phys. Soc. (London) **A63**, 213 (1950).

[43] B. Bleaney, Proc. Roy. Soc. (London) **A204**, 216 (1950).

[44] D. Bijl, Physica **8**, 497 (1941).

[45] R. J. Benzie, Proc. Phys. Soc. (London) **A64**, 507 (1951).

[46] de Klerk, Steenland, and Gorter, Phys. Rev. **78**, 476L (1950).

[46a] Darby, Hatton, Rollin, Seymour, and Silsbee, Proc. Phys. Soc. (London) **A64**, 861 (1951).

[47] W. J. de Haas and E. C. Wiersma, Physica **2**, 335 (1935).

[48] Casimir, de Haas, and de Klerk, Physica **6**, 365 (1939).

[49] Casimir, de Klerk, and Polder, Physica **7**, 737 (1940).

[50] N. Kürti and F. Simon, Proc. Roy. Soc. (London) **A149**, 152 (1935).

[51] de Klerk, Steenland, and Gorter, Physica **15**, 649 (1949).

[52] Steenland, de Klerk, and Gorter, Physica **15**, 711 (1949).

[53] A. H. Cooke, Proc. Phys. Soc. (London) **A62**, 269 (1949).

questionable in view of the multiple splitting of the ground state. In connection with these experiments the problem which is probably of greatest interest is the determination of the absolute thermodynamic temperature. The conventional method of determining this temperature is as follows: A magnetic temperature T^* is defined by extrapolation of Curie's law: $T^*=C/\chi$. The entropy is determined as a function of T^* by calculating (or measuring) the entropy prior to adiabatic demagnetization and measuring χ after demagnetizing. In calculating S it is necessary to consider the crystalline splitting of the energy levels and to apply demagnetization and local field corrections to the magnetic field strength. A curve of Q *versus* T^* is obtained by putting in known amounts of heat and measuring the change in T^*. It follows that the absolute temperature is given by $T=(dQ/dT^*)/(dS/dT^*)$. It is apparent that any other thermometric parameter could be used in place of T^*.

De Klerk, Steenland, and Gorter[43] have found that the real part of the susceptibility can be used as a thermometric parameter down to about 32 millidegrees on the magnetic scale where χ' has a maximum. The imaginary part of the susceptibility can be used between 3.9 and 4.4 millidegrees. KCr alum shows hysteresis effects below 0.004°K. For temperatures between 0.0037° and 0.0029°, De Klerk *et al.* were able to use the remanence as a thermometric parameter and it could have been used to still lower temperatures. In their later experiments[46] with a diluted salt they were able to use the T^* thermometer to the lowest temperatures attained.

SUMMARY

References have been made to a major portion of the experimental and theoretical research which has been done on the physical properties of chromium alums at low temperatures. An attempt has been made to point out where experimental work is incomplete and where theory is unsatisfactory. In the opinion of the writer the following experiments might serve as useful guides in revising, extending, or replacing existing theories:

1. Determination of the crystal structure of NH_4Cr alum below its transition temperature.
2. Extension of the relaxation measurements to frequencies higher than 100 Mc to determine to what extent the absorption is proportional to ν^2.
3. Paramagnetic relaxation measurements on supercooled NH_4Cr alum to ascertain the connection if any, between shattering and physical purity.
4. Microwave absorption measurements on salts of varying magnetic dilution to determine the importance of exchange coupling.
5. Measurements to very low temperatures of the thermal conductivity of an alum with the β-structure.
6. Extension of the observations on the relation between dilution and relaxation time.

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