

times artificial. An admolecule may indeed interact most strongly with the surface atoms in the vicinity of the adsorption site; the electronic structure of the latter, however, may nonetheless be modified by the rest of the metal and hence the adsorbate-metal bond need not be the same as that between the same adsorbate and a gas-phase cluster approximating the geometry of the adsorption site. Consequently small metal cluster "models" for the localized bonding will not always mimic the interaction with the surface accurately.

The situation therefore, as I see it, is as follows: The gross features of the chemisorptive bond, as well as that between a molecule and a very small cluster, are adequately described by a local bond. However, the chemistry and the spectroscopy, especially vibrational spectroscopy, may respond to subtle effects which are not always accurately understood by analogy with single-metal-atom or very small, stable cluster complexes. Moreover, catalysis by small, supported-metal aggregates will in general be different from that by stable cluster complexes as a result of the existence of many "metastable" structures for the bare cluster. When large enough to achieve a crystalline aspect,

further differences set in arising from substrate-mediated adsorbate interactions. On two-dimensionally periodic surfaces one might have additional collective effects as well.⁷⁰

Much of the above is speculative. It is nevertheless clear that a great number of phenomena have been reported which are unique to bulk metals having no obvious local counterparts. While their role in surface chemistry is as yet uncertain, it behooves us to investigate it.

I am indebted to my collaborators, particularly Dr. John E. Hulse and Mr. R. Smith, on whose work much of this account is based, and to the National Science and Engineering Research Council of Canada, The Research Corporation, Imperial Oil, and the Atkinson Foundation for financial support.

(70) Two recent angle-resolved UPS studies of xenon on Pd(100) (K. Horn, M. Scheffler, and A. M. Bradshaw, *Phys. Rev. Lett.*, **41**, 822 (1978)) and of CO on Pd(100) (A. M. Bradshaw, private communication) show convincing evidence of dispersion in the ordered two-dimensional adsorbate layer. These are the first examples of a direct manifestation of the two-dimensional periodicity, i.e. of two-dimensional Bloch states.

(71) G. Blyholder and M. C. Allen, *J. Am. Chem. Soc.*, **91**, 3158 (1969).

(72) M. Poliakoff and J. J. Turner, *J. Chem. Soc. A*, 2403 (1971).

(73) R. Whyman, *J. Chem. Soc., Dalton Trans.*, 1375 (1972).

(74) P. B. Johnson and R. W. Chisty, *Phys. Rev. B.*, **6**, 4370 (1972).

New Transparent Ferromagnets

PETER DAY

Oxford University, Inorganic Chemistry Laboratory, Oxford, OX1 3Q, England

Received September 14, 1978

This Account describes a wide-ranging set of experiments to prepare and characterize a new series of transport ionic ferromagnets with the general formulae A_2CrX_4 , where A is either an organic or an inorganic unipositive cation and X is a halide ion.

The large majority of ferromagnets are metallic conductors. Conversely, by far the largest proportion of ionic transition-metal or lanthanide compounds, including oxides, halides, sulfates, and many complexes, are antiferromagnets. In its simplest terms, ferromagnetism in metals arises from the coupling of localized electrons on neighboring centers, such as those in partly occupied 3d shells, via the mobile conduction electrons.¹ In insulators, the interaction between the unpaired electrons on neighboring cations is normally mediated by an intervening ligand bridge, usually an anion. In that case the sign of the resulting exchange integral depends on a variety of competing superexchange pathways involving delocalization of the unpaired spin on the metal toward the ligand as a result of covalency.² It turns out that in the great majority of cases the sum total of all the superexchange pathways is an antiferromagnetic coupling.

Peter Day was born at Wrotham, Kent, England, in 1938. His first degree and D.Phil. are from Oxford University, where he was a Scholar at Wadham College. At present he is a Science Research Council Senior Research Fellow and Fellow of St. John's College, Oxford, having, until 1977, been University Lecturer in Inorganic Chemistry. In 1971 he was awarded the Corday-Morgan Medal of The Chemical Society.

Are there then any ionic transition-metal salts which order as simple ferromagnets? The answer is very few. In fact, Table I contains close to an exhaustive list. A striking feature of this list³⁻¹¹ is how chemically disparate the various substances are, embracing simple cubic lattices, coordination complexes, and lanthanide and transition-metal compounds. Having such diverse crystal structures and ground-state electron configurations, it would be surprising if the superexchange pathways giving rise to the ferromagnetic ordering had very much in common. However, at least between the

(1) C. Zener, *Phys. Rev.*, **81**, 440 (1951).

(2) P. W. Anderson, *Phys. Rev.*, **79**, 350 (1950).

(3) H. L. Davis and A. Narath, *Phys. Rev. A*, **134**, 433 (1964).

(4) B. J. Matthias, R. M. Bozorth, and J. H. Van Vleck, *Phys. Rev. Lett.*, **7**, 160 (1961); J. R. McGuire and M. W. Shafer, *J. Appl. Phys.*, **35**, 984 (1964).

(5) C. A. Catanese, A. J. Skjeltorp, H. E. Meissner, and W. P. Wolf, *Phys. Rev. B*, **8**, 4223 (1973).

(6) A. N. Holden, B. T. Matthias, P. W. Anderson, and H. W. Lewis, *Phys. Rev.*, **102**, 1463 (1956); H. J. Buser, A. Ludi, P. Fischer, T. Studach, and B. W. Dale, *Z. Phys. Chem. (Frankfurt am Main)*, **92**, 354 (1974); B. Mayoh and P. Day, *J. Chem. Soc., Dalton Trans.*, 1483 (1976).

(7) I. Yamada, *J. Phys. Soc. Jpn.*, **33**, 979 (1972); W. Kleeman and Y. Farge, *J. Phys. (Paris), Lett.*, **35**, 135 (1974).

(8) L. J. De Jongh and W. D. Van Amstel, *J. Phys. (Paris), Collog.*, **1**, C1-880 (1971); L. J. De Jongh and A. R. Miedema, *Adv. Phys.*, **23**, 1 (1974).

(9) C. G. Barraclough, A. K. Gregson, and S. Mitra, *J. Chem. Phys.*, **60**, 962 (1974); H. Miyoshi, *J. Phys. Soc. Jpn.*, **37**, 50 (1974).

(10) W. M. Reiff and S. Foner, *J. Am. Chem. Soc.*, **95**, 260 (1973).

(11) W. P. Wolf, M. J. M. Leask, B. W. Mangium, and A. F. G. Wyatt, *J. Phys. Soc. Jpn., Suppl. B.*, **1**, 487 (1961).

Table I
Ionic Ferromagnets

	T_c/K	color	spin-forbidden crystal-field states	ref
CrBr ₃	33	red-purple	yes	3
EuO	69	black	no	4
Tb(OH) ₃	3.7	-	no	5
Fe[Fe(CN) ₆] ₃ · 14H ₂ O	5.5	blue-black	no	6
K ₂ CuF ₄	6.25	yellow	no	7
(RNH ₃) ₂ CuCl ₄	8-8	yellow	no	8
Mn-phthalocyanine	-	black	no	9
Fe(<i>o</i> -phenanthroline) ₂ Cl ₂	5	dark red	no	10
GdCl ₃	2.2	red	no	11
A ₂ CrX ₄	50-60	green	yes	this work

Cu^{II} examples and the Cr^{II} compounds there are some close analogies.

A significant word in the title of this Account is "transparent". Except in the thinnest sections metals are quite opaque to all visible and infrared frequencies, but insulators may have extended regions of transparency at frequencies lower than the band gap. Ligand-field and charge-transfer excited states are the commonest source of visible light absorption in the insulating ferromagnets, though in the two Eu examples the lowest excited states are most likely $4f \rightarrow 5d$.⁴ Like $f \rightarrow d$ transitions, charge-transfer transitions, being electric dipole allowed, result in absorption bands with peak linear absorption constants of some tens of thousands of cm^{-1} and also several thousand cm^{-1} wide. Compounds in which these bands appear in the visible are deeply colored or black. The energies of charge-transfer transitions depend on "optical electronegativities",¹² so there is little point in looking for compounds transparent in the visible when the metal is in a high oxidation state or the anion has a low electronegativity. Thus CrI₃ is black, and so is the mixed oxide Y₃Fe₅O₁₂, better known as YIG, which, although long famous as a transparent ferromagnet,¹³ is really neither appreciably transparent in the visible nor a true ferromagnet. It is actually ferrimagnetic because Fe(III) ions occupy both octahedral and tetrahedral sites.

When one is looking for visible transparency, therefore, it is better to choose compounds of metals in lower oxidation states with ligands of high electronegativity, such as the lighter halogens. Even then, spin-allowed ligand-field transitions need to be considered. They usually have peak linear absorption constants of a few hundred cm^{-1} and widths nearly as big as charge-transfer bands, and so can obscure much of the visible region. CrBr₃ is dark, not because of charge-transfer bands, but because the two broad ligand-field bands ${}^4A_{2g} \rightarrow {}^4T_{1g}$ and ${}^4A_{2g} \rightarrow {}^4T_{2g}$ overlap strongly.

Spin-forbidden ligand-field bands are not only weaker, but usually much narrower. In magnetic lattices, whether ferro- or antiferromagnetic, they also have an intrinsic interest because most of their intensity derives from creation or annihilation of spin waves (magnons) accompanying the electronic excitations, or excitons.¹⁴ The intensities, polarizations, and band shapes of such exciton-magnon combination bands thus

contain detailed information about the densities of states and dispersion of the excitons and magnons and the thermal populations of the magnon states, which are related directly to the ordering process.

So much for the wider background to our experiments on the tetrahalogenochromates. They provide important new examples of the small class of visibly transparent ferromagnetic compounds. Furthermore, they are unique in having well-resolved spin-forbidden crystal-field transitions in the visible, whose properties can be used to probe the magnetic excitations. Uniquely, too, these bands are the only ones in the visible. Consequently when the crystals go through their Curie temperature, they change color!

The binary phase diagrams ACl-CrCl₂, where A is K, Rb, Cs, were first determined by Siefert and Klatyk,¹⁵ who showed from X-ray powder patterns that in each case there were two compounds, ACrCl₃ and A₂CrCl₄. The former had the hexagonal perovskite structure, the latter the K₂NiF₄ structure. All the compounds had room temperature magnetic moments close to that expected for an $S = 2$ ground state. Later measurements at 80 K,¹⁶ however, gave slightly lower moments for the hexagonal perovskite phases, but very much larger ones for the ones with the K₂NiF₄ structures. Using the simple Curie formula a value of $11.3 \mu_B$ was calculated for the moment of Rb₂CrCl₄! Clearly this is much bigger than for any magnetically dilute d^n ground state and must mean that at 80 K the compound is on the point of becoming ferromagnetically ordered. Siefert and Klatyk reported that the A₂CrCl₄ salts were yellow-green, implying small visible absorption. From these facts it seemed that the compounds were additions to the select group of transparent ferromagnets.

Preparation and Crystal Growing

The published ACl-CrCl₂ phase diagrams¹⁵ show that the K₂CrCl₄ and Rb₂CrCl₄ phases are congruently melting while Cs₂CrCl₄ melts incongruently. In principle, therefore, crystals of the two former salts could be prepared by slowly cooling a melt of the alkali metal chloride and CrCl₂ with the correct stoichiometric composition. The simplest way of doing this is to seal the powdered material in a silica ampule and, after evacuating and carefully flaming it out, to heat it above the melting point in a vertical tube furnace and lower it slowly (1-2 mm/h) through a temperature gradient (Bridgman method). For optical measurements and elastic neutron scattering, crystals of a few millimeters on edge are sufficient, but for inelastic neutron scat-

(12) C. K. Jørgensen, "Orbitals in Atoms and Molecules", Academic Press, New York, 1962.

(13) R. Pauthenet, *Ann. Phys.*, **3**, 424 (1958); G. B. Scott, D. E. Lacklinton, and J. L. Page, *Phys. Rev. B*, **10**, 1971 (1974).

(14) D. Sell, R. L. Greene, and R. M. White, *Phys. Rev.*, **158**, 489 (1967).

(15) H. J. Siefert and K. Klatyk, *Z. Anorg. Allg. Chem.*, **334**, 113 (1964).

(16) L. F. Larkworthy and J. K. Trigg, *Chem. Commun.*, 1221 (1970).

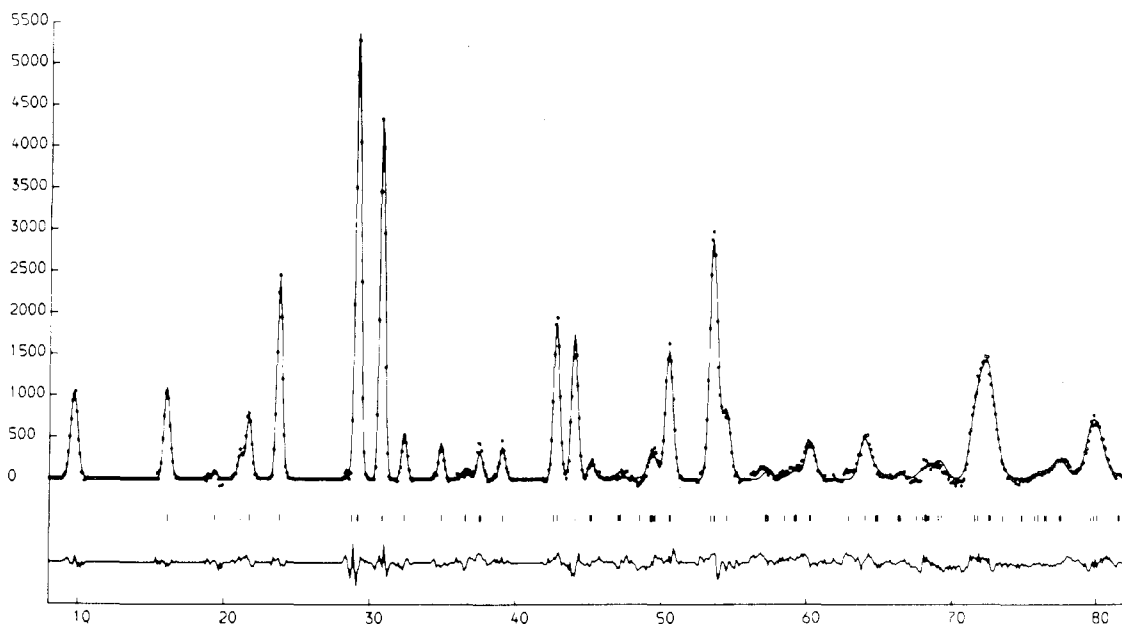


Figure 1. Powder neutron diffraction profile of Cs_2CrCl_4 at 4.2 K. The vertical lines show calculated peak positions and the lowest line in each case is the residual of the profile analysis.

tering one needs single crystals of at least 1 cm^3 . Furthermore, one's ability to measure spin waves close to the Brillouin zone center is determined by the width of the elastic scattering peaks, and hence by crystal perfection. A low mosaic spread is thus desirable. Large crystals suitable for inelastic neutron scattering experiments were grown by the Crystal Growing Group in the Clarendon Laboratory, Oxford, using the Czochralski method.¹⁷ Extreme care is needed to exclude oxygen and water from all stages in the preparation and crystal growing as the powdered Cr(II) chlorides are both hygroscopic and very easily oxidized. On the other hand the cleaved surfaces of larger single crystals remain shiny in air for some hours. However, all starting materials and crystals are handled exclusively under dry oxygen-free nitrogen. The CrCl_2 was prepared either from Cr and HCl or from CrCl_3 by reduction with Cr metal or Ga.¹⁸

More recently, we found that ferromagnetic compounds of the same general type can be made by replacing the group 1A cations by monoalkylammonium cations.^{19,20} Compounds with the general formula $(\text{RNH}_3)_2\text{CrCl}_4$ ($\text{R} = \text{CH}_3$ to $\text{C}_{12}\text{H}_{25}$) are not prepared from melts but by precipitation on slowly cooling an ethanol solution.

Crystal and Magnetic Structures

First experiments on the crystal and magnetic structures of A_2CrCl_4 salts used powder neutron diffraction.²¹ A powerful method of determining structures from powder neutron data is the Rietveld profile refinement method²² by which the structure is refined, not simply from the angles and intensities of the diffraction peaks, but by treating each individual data point, as the diffraction profile is scanned in 0.1° steps, as a separate item of input to the least-squares re-

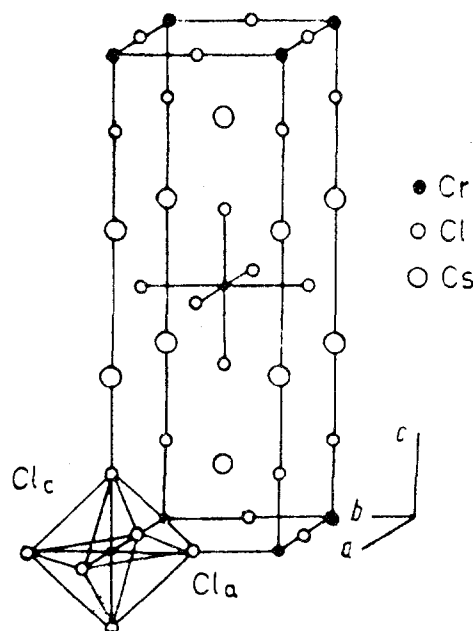


Figure 2. The K_2NiF_4 structure.

finement process. Figure 1 shows the diffraction profile of Cs_2CrCl_4 at 4 K with, underneath, the residual of the least-squares fit represented by the full line through the data points. By comparing the 4 K profile with one measured at 300 K, a simple indication of the fact that the compound is ferromagnetically ordered is that no purely magnetic peaks appear in the 4 K profile; the magnetic cell coincides with the crystallographic cell.

The powder diffraction profiles of Rb_2CrCl_4 and Cs_2CrCl_4 index in the D_{4h}^{17} space group, the same as K_2NiF_4 (Figure 2). Since K_2CrCl_4 has an orthorhombic unit cell and Cs_2CrCl_4 is incongruently melting, most of our detailed structural experiments centered on the Rb salt, which is both tetragonal and congruently melting, so that single crystals can be grown. Single-crystal diffraction measurements were needed for three reasons. First, the powder profiles were not unambiguous regarding the direction of the magnetic mo-

(17) P. J. Walker and G. Garton, *J. Cryst. Growth*, **36**, 351 (1976).

(18) G. Garton and P. J. Walker, *J. Cryst. Growth*, **33**, 331 (1976).

(19) C. Bellitto and P. Day, *J. Chem. Soc., Chem. Commun.*, 870 (1976).

(20) C. Bellitto and P. Day, *J. Chem. Soc., Dalton Trans.*, 1207 (1978).

(21) M. T. Hutchings, A. K. Gregson, P. Day, and D. H. Leech, *Solid State Commun.*, **15**, 313 (1974).

(22) H. M. Rietveld, *J. Appl. Crystallogr.*, **2**, 65 (1969).

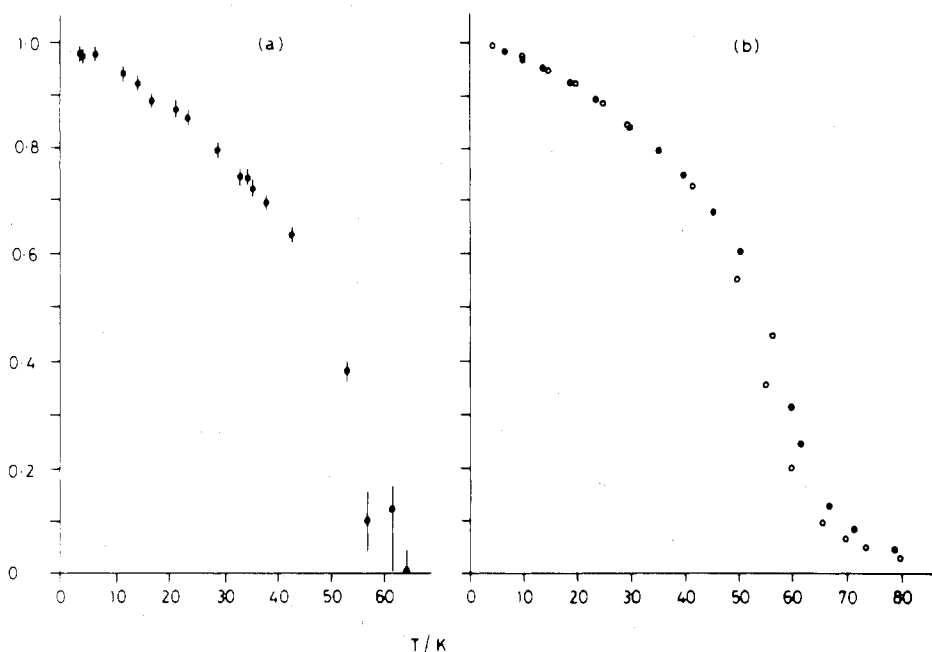


Figure 3. Temperature variation of magnetization of Rb_2CrCl_4 from (a) neutron diffraction and (b) susceptibility measurements.

ment: with a single crystal the intensities of (101) and (004) peaks were therefore measured with a magnetic field of 1.8 T applied perpendicular to the scattering plane, which coincided with the (010) plane of the crystal.²³ The diffracted intensity is proportional to $\sin^2 \alpha$, where α is the angle between the moment and the scattering vector. Within experimental error $\alpha(004)$ was constant at 90° , that is, the moments lie in the basal plane, within which they are rotated by the applied field.

The second reason for carrying out single-crystal neutron diffraction was to determine the variation of the magnetization with temperature. Whereas measurements of magnetization by susceptibility methods require a magnetic field, the magnetic contribution to the elastic neutron scattering intensity is a direct measure of the spontaneous (zero-field) magnetization. Integrated intensities of (002), (101), and (004) were recorded from liquid helium temperature up to 90 K; we found that the Curie temperature of Rb_2CrCl_4 was 57 ± 2 K. To subtract the nuclear contribution to the total scattering, we used the intensities recorded above T_c , and found the variation in magnetization with temperature (Figure 3a). It should be compared with the magnetization curves measured with a Faraday susceptibility balance (Figure 3b).

Finally, only single-crystal measurements could reveal the more subtle features of the structure. As we have noted, powder X-ray and neutron diffraction suggested a K_2NiF_4 structure for Rb_2CrCl_4 . Best values of the positional parameters for the Cl atoms obtained in this way require that the coordination around the Cr atoms be that of an octahedron flattened along the tetragonal c axis. Cr^{2+} is formally $3d^4$, and hence in octahedral coordination should be subject to a strong Jahn-Teller distortion. The situation here is very analogous to that obtaining in K_2CuF_4 . For many years the latter was thought to be the only example of a Cu^{2+} compound in which the tetragonal Jahn-Teller distortion was a

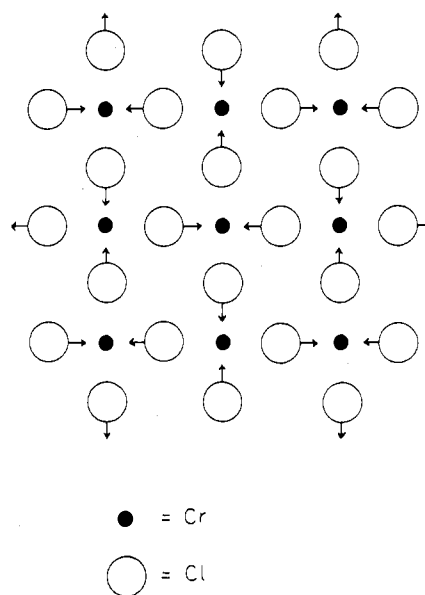


Figure 4. Jahn-Teller distortion within the basal plane of K_2CuF_4 and Rb_2CrCl_4 .

flattening rather than an elongation.²⁴ Recently, however, it has been established that the structure contains an antiferro-distortive displacement of the F atoms away from the centers of the lines joining each pair of Cu atoms in the basal plane, so that the coordination around each Cu is tetragonally elongated. The principal axes of all the CuF_6 units lie within the basal plane, but at right angles to one another (Figure 4). Clearly such a possibility must be considered in Rb_2CrCl_4 . A search for reflections which would be allowed in the D_{2d}^{10} space group, the one proposed for K_2CuF_4 by Haegele and Babel,²⁵ revealed nothing, but a more recent proposal²⁶ suggests a different ordering of the distorted planes in K_2CuF_4 . Weak reflections

(24) For example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed., Interscience, New York, 1966, p 899.

(25) R. Haegele and D. Babel, *Z. Anorg. Allg. Chem.*, 409, 11 (1974).

(26) Y. Ito and J. Akamitsu, *J. Phys. Soc. Jpn.*, 40, 1333 (1976).

(23) M. J. Fair, A. K. Gregson, P. Day, and M. T. Hutchings, *Physica (Utrecht)*, 86-88B, 657 (1977).

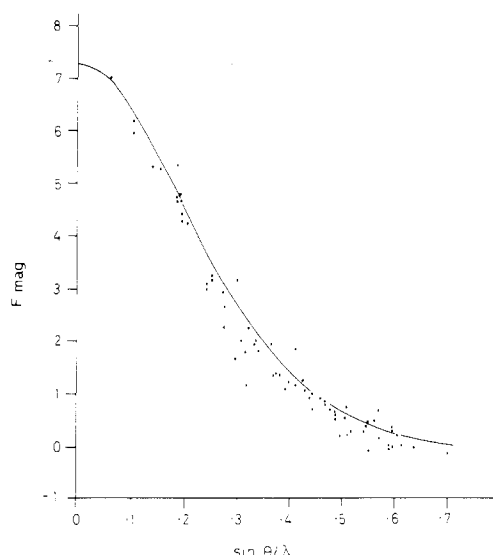


Figure 5. Magnetic form factor of Cr^{2+} from polarized neutron diffraction of Rb_2CrCl_4 . The full line is the calculated form factor³² scaled to $3.6 \mu_B$.

compatible with this new suggestion have now been observed in Rb_2CrCl_4 .²⁷ Independent confirmation that the lattice contains two Jahn–Teller distorted metal ion sites with their principal axes at right angles within the basal plane comes from the angular variation of the resonance frequency in the ^{53}Cr NMR spectrum.²⁸

A further structural aspect concerns the unpaired spin distribution. A powerful method for determining spacial distributions of unpaired spin density in magnetic crystals is the diffraction of polarized neutrons by the lattice of aligned spins.²⁹ While the cross section for magnetic scattering depends on the angle between the neutron spin and the electron spin, nuclear scattering is independent of this angle. Consequently by measuring the intensity of a reflection when the neutron and electron spins are first parallel, then antiparallel, the nuclear contribution to the scattered intensity is eliminated. Fourier transformation of the purely magnetic reflection intensities then gives the unpaired spin density distribution in the unit cell. To carry out such an experiment the unpaired electron spins have to be aligned. While this can be done for a magnetically dilute compound by applying a big enough external field at a low enough temperature, the experiment can obviously be done more effectively on substances having a spontaneous magnetization, ferromagnets, ferrimagnets, or canted antiferromagnets.

Leaving aside experiments on ferromagnetic alloys, only a handful of inorganic compounds have so far been examined by polarized neutron diffraction.³⁰ At the I.L.L. high flux reactor we collected polarization data on 102 independent reflections of Rb_2CrCl_4 at 4.2 K, measuring polarization ratios of the $(h0l)$ peaks to $\sin \theta/\lambda = 0.6$ at two different neutron wavelengths, to check for extinction.³¹ Our spin-density map is not complete yet, but Figure 5 shows a comparison between the

(27) M. T. Hutchings and E. Janke, personal communication.

(28) K. Le Dang, P. Veillet, and P. J. Walker, *J. Phys. (Paris)*, C, 10, 4593 (1977).

(29) W. Marshall and S. W. Lovesey, "Theory of Thermal Neutron Scattering", Clarendon Press, Oxford, 1971.

(30) For a well-documented recent example see F. A. Wedgwood, *Proc. R. Soc. London, Ser. A*, 349, 447 (1976).

(31) M. J. Fair, J. B. Forsyth, and P. Day, *I. L. L. Annu. Rep.*, 149 (1975).

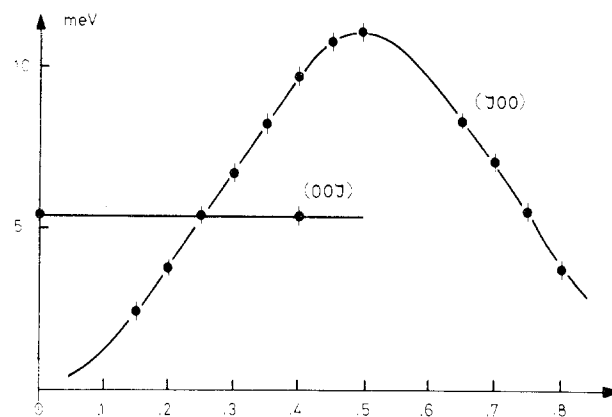


Figure 6. Dispersion of magnons propagating in the basal plane (100) and along the c axis (001) of Rb_2CrCl_4 at 5 K. The lines through the experimental points are the best fit to eq 1 with $J_1 = 5.3 \pm 0.1 \text{ cm}^{-1}$ and $D = 0$.³⁸

observed magnetic form factor and one computed theoretically³² for Cr^{2+} , scaled to $3.7 \mu_B$.

Magnetic Susceptibility and Magnetization

First we measured the susceptibilities and magnetizations of the three compounds A_2CrCl_4 ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) to 4 K, using powder samples and a Faraday balance.³³ We also repeated the earlier susceptibility measurements from 77 K to room temperature^{34,35} to fit them to a high-temperature series expansion^{36,37} and hence calculate the near-neighbor exchange constants.

The large positive Weiss constants (70–80 K) indicate qualitatively that the compound must be ferromagnetic. Best fit to the series expansion are given by positive exchange constants J in the range $3.5\text{--}4.5 \text{ cm}^{-1}$ and g values close to 2. However, inelastic neutron scattering measurements of the spin-wave dispersion can provide much more precise estimates of J . The variation with temperature of the magnetization curve was obtained from neutron diffraction. The applied field in the magnetic experiment rounds off the phase transition, making it harder to get an accurate estimate of T_c . The value obtained in this way for Rb_2CrCl_4 ($62 \pm 2 \text{ K}$) is a little higher than that found by neutron diffraction.

Inelastic Neutron Scattering

The ultimate stage in characterizing the magnetic parameters of a new substance is to measure the dispersion relations of its magnons, preferably as a function of temperature up to T_c . Coherent inelastic neutron scattering measurements on Rb_2CrCl_4 were made on the Pluto triple axis spectrometer at Harwell³⁸ and the IN2 and IN8 instruments at the I.L.L.³⁹ To record the very small energy and momentum transfers from magnons close to the zone center, a long wave-

(32) E. J. Lisher and J. B. Forsyth, *Acta Crystallogr., Sect. A*, 27, 545 (1971).

(33) A. K. Gregson, P. Day, D. H. Leech, M. J. Fair, and W. E. Gardner, *J. Chem. Soc., Dalton Trans.*, 1306 (1975).

(34) D. H. Leech, Ph.D. Thesis, Manchester, 1971.

(35) D. H. Leech and D. Machin, *J. Chem. Soc., Chem. Commun.*, 866 (1974).

(36) G. S. Rushbrooke and P. J. Wood, *Mol. Phys.*, 1, 257 (1958).

(37) M. E. Lines, *J. Phys. Chem. Solids*, 31, 101 (1970).

(38) M. T. Hutchings, M. J. Fair, P. Day, and P. J. Walker, *J. Phys. (Paris)*, C, 9, L55 (1976).

(39) M. J. Fair, M. T. Hutchings, P. Day, R. Ghosh, and P. J. Walker, *J. Phys. (Paris)*, C, 11, L813 (1978).

length triple axis instrument at the Danish Atomic Energy Research Establishment, Risø, has also been used.⁴⁰

If we add an anisotropy term $D_i \sum_i S_i^z$ to the Heisenberg Hamiltonian, the spin wave energies are given³⁸ by

$$h\omega_q = 2S\{[J(0) - J(q)][J(0) - J(q) + D]\}^{1/2} \quad (1)$$

where

$$J(q) = \sum_{i,r} J_i \exp(iqr_i) \quad (2)$$

the sum being taken over the i nearest neighbor ions positioned at r_i . Experimental spin wave energies, shown in Figure 6, were least-squares-fitted to eq 1 to give values of J_1 , the nearest neighbor exchange constant, and D . J_1 was estimated as $5.3 \pm 0.1 \text{ cm}^{-1}$, a much more precise value than the one obtained from the series expansion. Two points about Figure 6 are noteworthy: first, the value of D which gave the best fit to the spin-wave dispersion in the basal plane was zero, and second, there was no detectable dispersion of the spin waves propagating along the c axis, equivalent to zero J between successive layers. The K_2NiF_4 structure is a layer lattice, but both observations focus attention on the three-dimensional ordering mechanism. Thus Mermin and Wagner⁴¹ have given a rigorous theoretical proof that a two-dimensional lattice with purely Heisenberg interactions cannot undergo a phase transition to an ordered state at any non-zero temperature, although in practice this could be relaxed by introducing anisotropy or an interaction between the planes.⁴² Experiment suggests that both the in-plane anisotropy and the interplanar interaction must be very small, yet Rb_2CrCl_4 orders at 63 K. The dilemma has been resolved by further neutron-scattering experiments with a particularly good crystal having a low mosaic spread. Because the boule used to obtain the results in Figure 6 consisted of several slightly misaligned domains, measurements could only be made down to $q = 0.15$. New measurements⁴⁰ at lower q reveal that the dispersion curve does not go to zero energy at $q = 0$, but to approximately 0.7 cm^{-1} , equivalent to about 1 K.

Optical Properties

Expectation of finding unusual optical properties was a substantial driving force in our preoccupation with these ionic ferromagnets. The ground term of a $3d^4$ ion in an octahedral ligand field would be 5E_g , with only one other quintet term, ${}^5T_{2g}$, in the manifold of ligand-field states. However, the relevant Tanabe-Sugano diagram⁴³ shows a large number of triplet terms which, for all reasonable values of the ligand-field splitting parameter Δ and the Racah parameter B , are at higher energies than the quintet. Almost all 6-coordinate Cr(II) compounds have a strong Jahn-Teller distortion, splitting the E and T_2 terms, but in general the absorption corresponding to ${}^5E_g \rightarrow {}^5T_{2g}$ is an envelope of overlapping bands in the near-infrared. Transitions to the various triplets are found across the visible and

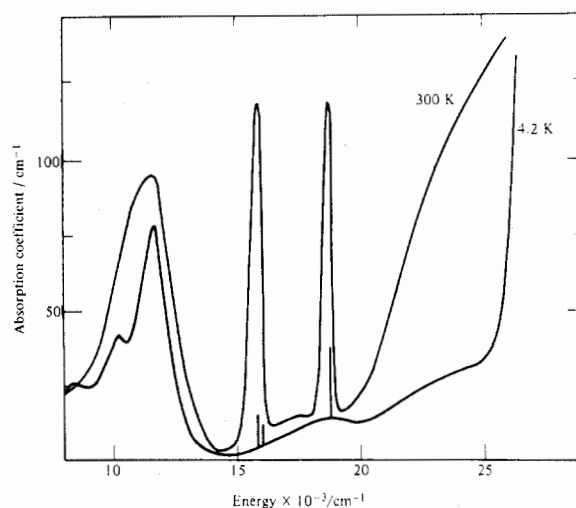


Figure 7. Absorption spectrum of K_2CrCl_4 at 300 K and 4 K with unpolarized light incident parallel to the c axis.⁴⁴

since Cr(II) has a low optical electronegativity the intense absorption edge resulting from ligand-to-metal charge transfer is on the edge of the ultraviolet.

Figure 7 shows the transmission spectrum of K_2CrCl_4 at room temperature and at 4.2 K.⁴⁴ In the visible only two of the anticipated triplet states appear, but they are sharp and well resolved even at room temperature. On lowering the temperature, a remarkable change occurs: in the near-infrared the group of bands assigned to the spin-allowed ligand-field transitions diminish a little because most of their intensity comes from vibronic coupling; in the visible though, the two spin-forbidden bands all but vanish! To our knowledge no such effect had ever been observed before; it can be seen with the naked eye since the two bands in question provide the only absorption in the visible region, and removing them changes the crystal from dark olive green to pale yellow. At low temperatures the chloromagnets are therefore easily the most transparent ferromagnets known. The Rb and monoalkylammonium salts behave in the same way.⁴⁵

Such behavior poses two questions. Why, out of the large number of possible triplet transitions, are there only two with appreciable intensity? And why does their intensity vary so much with temperature? To answer the first question ligand-field calculations were carried out over a wide region of parameter space involving Δ , B , and a tetragonal field component.⁴⁶ In the relevant part of the d^4 Tanabe-Sugano diagram for O_h symmetry we find ${}^3T_{1g}$, 3E_g , ${}^3T_{1g}$, and ${}^3T_{2g}$ from 3H , ${}^3A_{2g}({}^3F)$, and ${}^3A_{1g}({}^3G)$. Of these, ${}^3E_g({}^3H)$ and ${}^3A_{1g}({}^3G)$ do not vary with Δ ; i.e., in the strong field limit they are pure "spin flips". A similar conclusion is reached on applying a tetragonal perturbation which splits the 5E_g ground state into ${}^5B_{1g}$ and ${}^5A_{1g}$. Transitions which do not involve any changes in orbital occupancy, for instance the well-known ${}^4A_{1g}$, 4E_g bands of Mn(II) compounds,⁴⁷ are always narrow because they do not change the molecule's potential-energy surface. Furthermore, in a variety of d^4 compounds, whether ferromagnetic or antiferromagnetic (e.g., binary and

(40) J. Als-Neilsen, M. T. Hutchings, and P. A. Lindgard, personal communication.

(41) N. D. Mermin and H. Wagner, *Phys. Rev. Lett.*, **17**, 1133 (1966).

(42) For example, M. E. Lines, *Phys. Rev.*, **B**, **3**, 1749 (1971).

(43) B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, 1967, p 162.

(44) P. Day, A. K. Gregson, and D. H. Leech, *Phys. Rev. Lett.*, **30**, 19 (1973).

(45) C. Bellitto and P. Day, *J. Chem. Soc., Chem. Commun.*, 511 (1978).

(46) A. K. Gregson, unpublished.

(47) L. E. Orgel, *J. Chem. Phys.*, **23**, 1824 (1955).

ternary Cr(II) fluorides^{48,49} and chlorides,³⁴ CrI₂⁵⁰ and MnF₄,⁵¹ there are two relatively intense spin-forbidden bands between 15 000 and 20 000 cm⁻¹. Using magnetic circular dichroism, which is much more sensitive to weak transitions than ordinary absorption spectroscopy, we also located the baricenters of other cubic field components of ³H and ³G.⁵²

The most interesting question, however, concerns the temperature dependence. In magnetic insulators spin-forbidden ligand-field transitions gain intensity by coupling to spin fluctuations in the ordered lattice. Qualitatively the decrease in the crystal's spin projection when one of the ions undergoes a transition from a quintet to an excited triplet state is compensated either by creating a positive spin deviation within the array of ions remaining in their ground states or by annihilating a thermally excited negative deviation.⁵³ The former process is very well-known in antiferromagnets.⁵⁴ In ferromagnets only the latter process contributes to the absorption because, in proportion as the lattice is magnetized, no positive spin deviation, further increasing the spin projection of the lattice, is possible. Thus the intensity of an exciton-magnon combination band in a ferromagnet depends on the thermal population of magnons. Quantitatively:

$$I(\omega) = \sum_k I_k(\omega) = \sum_k |M_k|^2 \langle n_k \rangle \delta(\hbar\omega + E_k - \lambda_k) \quad (3)$$

where the summation is over the Brillouin zone, M_k is the electric dipole transition moment, $\langle n_k \rangle$ is the thermal population of magnons with the same wave-vector as the exciton, E_k is the energy of the magnon, λ_k is that of the exciton and the δ function ensures equality between the photon energy and the sum of the exciton and magnon energies.¹⁴ At thermal equilibrium $\langle n_k \rangle$ is given by the Planck distribution

$$\langle n_k \rangle = [\exp(E_{sw}/k_B T) - 1]^{-1} \quad (4)$$

and the total number of magnons excited at temperature T is

$$\sum_k \langle n_k \rangle = \int D(\omega) \langle n(\omega) \rangle d\omega \quad (5)$$

$D(\omega)$ being the magnon density of states in frequency units. Both $D(\omega)$ and E_{sw} are experimentally accessible from inelastic neutron scattering, but as a rough approximation we could take just the magnons close to the zone center, since only these are populated at low temperatures. For a two-dimensional easy-plane ferromagnet with negligible anisotropy the limiting form⁵⁵ of the magnon dispersion at small k is $E_{sw} \propto k^2$. When this approximation is used in eq 4 and 5 to calculate $\langle n_k \rangle$ and $D(\omega)$ and the results are substituted in eq 3, the integrated intensity of our exciton-magnon bands should vary at low temperature as T^2 , as shown in Figure 8 for the 530-nm band of Rb₂CrCl₄.⁵⁶ Note,

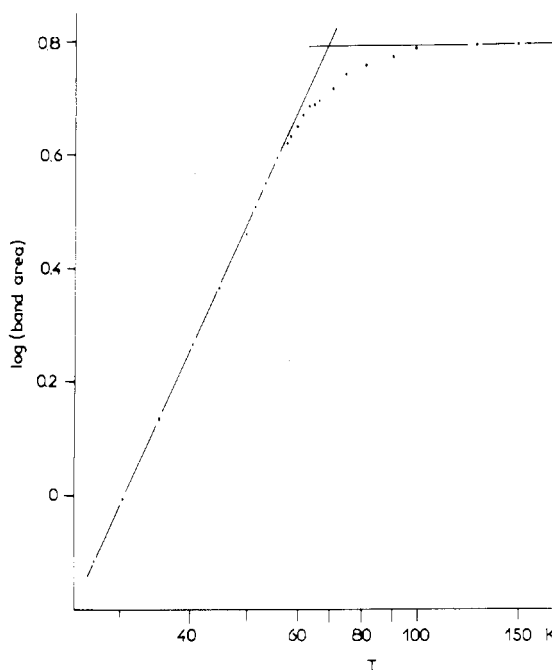


Figure 8. Intensity of the 530-nm absorption band in Rb₂CrCl₄ as a function of temperature.⁵⁶

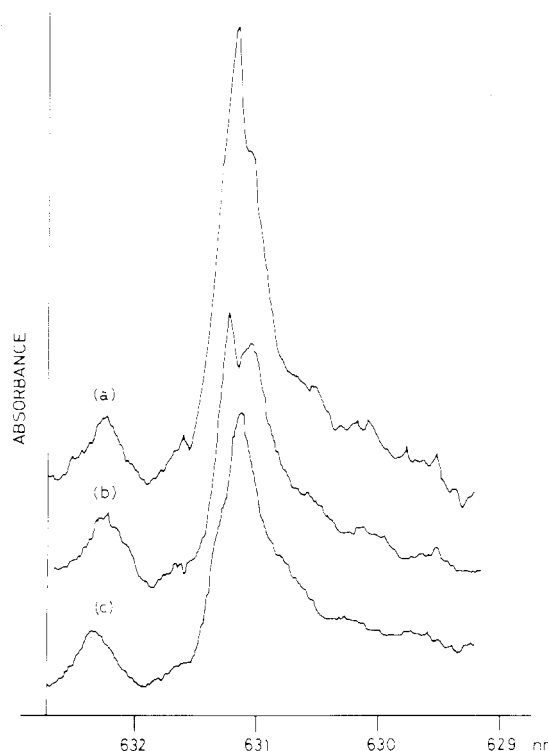


Figure 9. Axial absorption spectrum of Rb₂CrCl₄ in the 630-nm region at very low temperatures.⁵⁸ (a) 1.38 K, (b) 1.15 K, (c) 0.83 K.

however, that the T^2 dependence persists almost up to T_c and also that even above T_c the intensity continues to grow, presumably because short range order still persists. Strictly speaking, one should perform the integration in eq 3 over the whole Brillouin zone using magnon dispersion relations which are either obtained experimentally or fitted to the observed exchange parameters. This we have done for K₂CrCl₄,⁵⁷ and

(56) P. Day, *Collog. Int. C.N.R.S.*, **255**, 237 (1977).

(57) A. K. Gregson, P. Day, A. Okiji, and R. J. Elliott, *J. Phys. (Paris)*, **C, 9**, 4497 (1976).

(48) A. Earnshaw, L. F. Larkworthy, and K. S. Patel, *J. Chem. Soc. A*, 363 (1966).

(49) W. W. Holloway and M. Kestigian, *Spectrochim. Acta*, **22**, 1381 (1966).

(50) S. Jermin, Chemistry Part II Thesis, Oxford, 1972, unpublished.

(51) R. J. H. Clark, *J. Chem. Soc.*, 417 (1964).

(52) M. J. Fair, Chemistry Part II Thesis, Oxford, 1973, unpublished.

(53) For a review, see D. S. McClure in "Optical Properties of Ions in Solids", B. di Bartolo, Ed., Plenum, New York, 1975, p 259.

(54) K. Shinagawa and Y. Tanabe, *J. Phys. Soc. Jpn.*, **30**, 1280 (1971).

(55) D. J. Robbins and P. Day, *J. Phys. (Paris)*, **C, 9**, 867 (1976).

found good agreement with experiment from 4.2 K upward.

If there is a gap in the magnon spectrum at $k = 0$, as suggested by neutron scattering, the intensity of the optical absorption bands should begin to deviate from the T^2 law as the temperature becomes comparable to the gap energy. We therefore measured the sharp 632-nm band down to the limit of pumped ^4He , about 0.7 K.⁵⁸ Some of the results, obtained using a nitrogen laser pumped tunable dye laser⁵⁹ are shown in Figure 9. The sharp band at 631.3 nm, which dominates the band envelope at 3 K and upward, disappears rapidly below 1 K and can be quantitatively fitted to a gap energy equivalent to 1.0–1.5 K.

From these experiments we now have a good picture of the crystal and magnetic structures of the chlorochromates, the reasons why they are ferromagnetic, and the effect this has on their optical properties. Although

(58) P. Day, E. Janke, T. E. Wood, and D. R. Woodward, *J. Phys. C*, **12**, L329 (1979).

(59) C. Ironside, K. Gardner, D. R. Woodward, P. Day, and R. G. Denning, to be published.

they are the most visible transparent ferromagnets known at present, their relatively low Curie temperatures will limit technological application of their curious properties, whether to optical modulation or to magnetic data storage with optical readout. Nevertheless they have provided intriguing problems for magnetic theory and an object lesson in applying a wide range of physical techniques. A further dimension of chemical variation, only touched on in this account, concerns replacement of the alkali metal cations by organic groups, increasing the spacing between the layers up to as much as 25 Å.²⁰ With their simpler prototypes they too are good examples of how preparative inorganic chemistry can bring forward new systems to challenge the skills both of the experimental and of the theoretical physicist.

The experiments described here were carried out in collaboration with many colleagues, postdoctorates, and graduate students whose names appear in the references; my best thanks for all their help. Our group has been supported by the U.K. Science Research Council, A.E.R.E. Harwell, and the National Research Development Corporation.

Nonequilibrium Thermodynamics and the Stability of States Far from Equilibrium

JOEL KEIZER¹

Laboratory of Molecular Biology, National Institute of Arthritis, Metabolism and Digestive Diseases, National Institutes of Health, Bethesda, Maryland 20205

Received December 21, 1978

At equilibrium the three laws of thermodynamics—energy conservation, entropy maximization, and the inaccessibility of absolute zero—are the basis for understanding many relationships between experimental quantities.² Unfortunately, many of these relationships are valid only at equilibrium, since the Second Law is valid only for changes which end up at equilibrium.

In fact, a central problem in physical chemistry is this: Does there exist a generalization of the Second Law which is valid away from equilibrium? This is an old question having its origins in Boltzmann's work in gas kinetics,³ and many attempts have been made at answering it.⁴ In this Account, I will discuss a solution to this problem which is based on the dynamics of molecular fluctuations.⁵ These fluctuations are caused by the relentless motion involved in molecular processes and are intimately related to the stability of nonequilibrium systems.

The chief focus of this Account is nonequilibrium steady states⁶ of large collections of molecules. These

are states which have time-independent properties, even though mass, energy, or momentum is being transported through the system. Such states are in many ways like equilibrium states, yet they cannot be described by classical thermodynamics. Simple examples are the steady flow of fluid through a pipe or the steady dc current in an electrical resistor. More intricate, and fascinating, examples include systems which become unstable or begin to oscillate as the steady state is removed farther from equilibrium. Typical of these systems are the roll structure of Bénard cells in a layer of fluid heated from below,⁷ oscillating colors due to periodic changes in indicator concentrations in the Belousov reaction,⁸ or the periodic voltage and shape

(1) Permanent address: Department of Chemistry, University of California, Davis, CA 95616.

(2) E. Fermi, "Thermodynamics", Dover, New York, 1956.

(3) L. Boltzmann, "Lectures on Gas Theory", S. G. Brush, Translator, University of California Press, Berkeley, 1964.

(4) E. T. Jaynes, *Phys. Rev.*, **106**, 620 (1957); **108**, 171 (1957); M. J. Klein and P. H. E. Meijer, *ibid.*, **96**, 250 (1954); T. L. Hill, *Proc. Natl. Acad. Sci. U.S.A.*, **55**, 1381 (1966); P. Glansdorff and I. Prigogine, *Physica*, **30**, 351 (1964); R. Graham in "Quantum Statistics in Optics and Solid State Physics", Springer, Berlin, 1973; F. Schlögl, A. Stahl, R. Bausch, *Z. Phys.*, **187**, 290 (1965); C. W. Gardiner, *J. Chem. Phys.*, in press; F. Jähnig and P. Richter, *ibid.*, **64**, 4656 (1976); F. Hofelich, *Z. Phys.*, **226**, 395 (1969).

(5) J. Keizer, *J. Chem. Phys.*, **63**, 398 (1975).

(6) J. Keizer, *J. Chem. Phys.*, **65**, 4431 (1976).

(7) S. Chandrasekhar, "Hydrodynamic and Hydromagnetic Stability", Clarendon, Oxford, 1961.

Joel Keizer is Professor of Chemistry at the University of California, Davis, and, while this Account was written, a Visiting Scientist at the NIH. A graduate of Reed College (B.A.) and the University of Oregon (Ph.D.), he has long been interested in kinetic and thermodynamic descriptions of physical processes. He was a postdoctoral fellow at the Battelle Institute, 1969–1971, and a Gastdozent at the Freie Universität in Berlin in 1972. Since 1971 he has been on the faculty at Davis. He is an Associate Editor of *Accounts of Chemical Research*.