Å from the silver surface gives an interatomic I-Ag distance of 2.8 Å which is the same as in the AgI crystal. Within our scheme, this distance could be determined with 5% accuracy.

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Optical Properties of Ferromagnetic K_2CrCl_4

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The optical absorption spectrum of the ferromagnetic insulator K_2CrCl_4 has been measured from 8000 to 25 000 cm^{-1} and for temperatures between 4.2 and 300°K.

Ferromagnetic materials having discrete optical absorption bands, and hence regions of relative transparency in the visible, are rather uncommon. Indeed, in all the insulating ferromagnetic transition-metal compounds examined hitherto, the entire visible region is covered by a succession of broad overlapping ligand-field[1] or charge-transfer[2] bands. We now report preliminary optical studies of the three-dimensional ferromagnet K_2CrCl_4, the visible absorption of which is almost entirely concentrated into two narrow spectral regions, sufficiently resolved from each other to permit quantitative measurements of the temperature variation of their oscillator strengths.

K_2CrCl_4 is a member of an extensive series of ternary halides formed by alkali metals and divalent 3*d* elements.[3,4] X-ray powder photographs[3] indicated a structure very similar to that of Cs_2CrCl_4, which has the K_2NiF_4 structure. This conclusion is confirmed by a single-crystal x-ray study,[5] which demonstrated that the unit cell is in fact orthorhombic ($a = 7.13$, $b = 7.34$, $c = 14.97$ Å), though the deviation from the tetragonal cell of the parent K_2NiF_4 structure is small. The magnetic susceptibility of a powder sample measured between 80–300°K has been extrapolated to give a Weiss constant of $+67 \pm 1$°K.[3] Further analysis[3,6] of the same data using high-temperature series-expansion techniques[7,8] applicable to a Heisenberg ferromagnet having a plane square lattice with $S = 2$ yielded an exchange integral of 5.0 ± 0.5 cm^{-1}. Magnetization measurements over the range 4.2-80°K[9] confirm that the compound becomes ferromagnetic below 65°K.

Crystals of K_2CrCl_4 were grown from the melt in a Bridgman furnace. Because the plane of easy cleavage is perpendicular to the *c* axis, and thin crystals were needed for measurements of the two intense sharp visible transitions, good quality spectra were only obtained for light propagated along this axis (Fig. 1). Poorer-quality spectra recorded with the incident light perpendicular to *c* showed that while the axial and σ spectra were very similar, the π absorption was much weaker.[10] By comparison with other Cr(II) spectra,[11] we assign the three broad bands between 8000 and 14 000 cm^{-1} to the low-symmetry components of ^5D. If, in common with all other Cr(II) salts having strongly Jahn-Teller distorted ground states, we assume that the Cr site in K_2CrCl_4 is tetragonally elongated, the three bands are assigned to transitions from $^5B_{1g}(^5E_g)$ to $^5A_{1g}(^5E_g)$ and $(^5B_{1g} + {}^5E_g)(^5T_{2g})$.

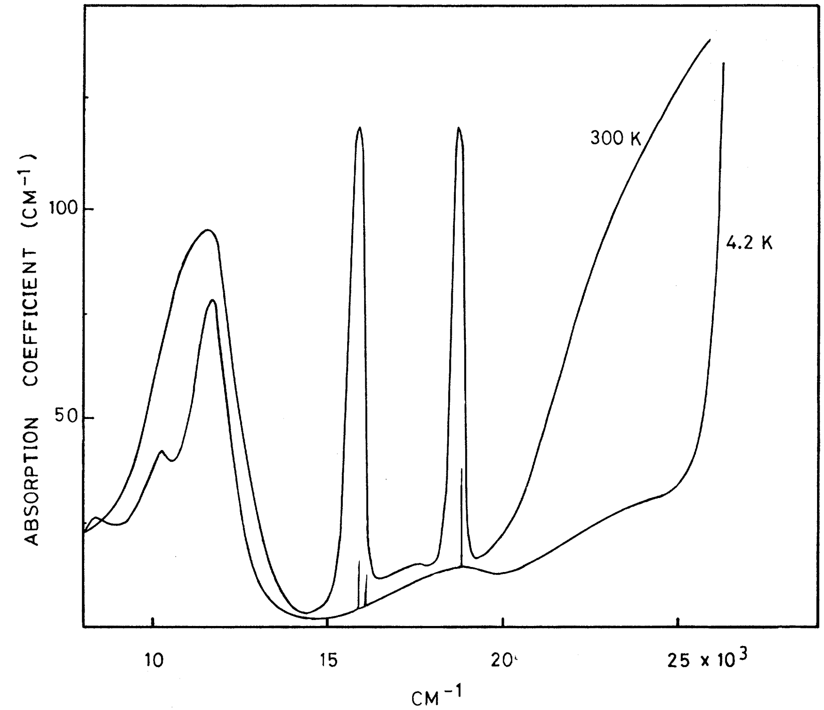

FIG. 1. Absorption spectra of a crystal of K_2CrCl_4 at 300 and 4.2°K. The incident light is propagated parallel to the c axis.

The most remarkable features in the optical spectrum of K_2CrCl_4 at 300°K are the two intense narrow lines at 15 900 and 18 700 cm^{-1}. They are much more intense relative to the quintet transitions than is normally observed in Cr(II) salts. Apart from these two lines, there are no other discrete absorption maxima in the visible region except for a weak and very ill-defined peak at about 17 500 cm^{-1}. Even more remarkable is the behavior of the two narrow lines on lowering the temperature. As indicated in Fig. 1, at 4.2°K the intensity of the lines all but disappears. The band at 15 900 cm^{-1} collapses to an extremely narrow line at 15 892 cm^{-1} together with another, slightly broader line at 16 062 cm^{-1}. The band at 18 700 cm^{-1} becomes a narrow doublet, centered at 18 726 cm^{-1}, with a splitting of 21 cm^{-1}. As the temperature is raised, all the narrow lines increase in intensity, and further lines appear at 16 215 cm^{-1} and 18 690 cm^{-1} when the temperature reaches about 23°K. At liquid-nitrogen temperature all the lines have coalesced into the two band envelopes seen at room temperature. The detailed temperature variation of the total oscillator strength of the 15 900 cm^{-1} transition is shown in Fig. 2. The inset in this figure indicates that the limiting behavior of the oscillator

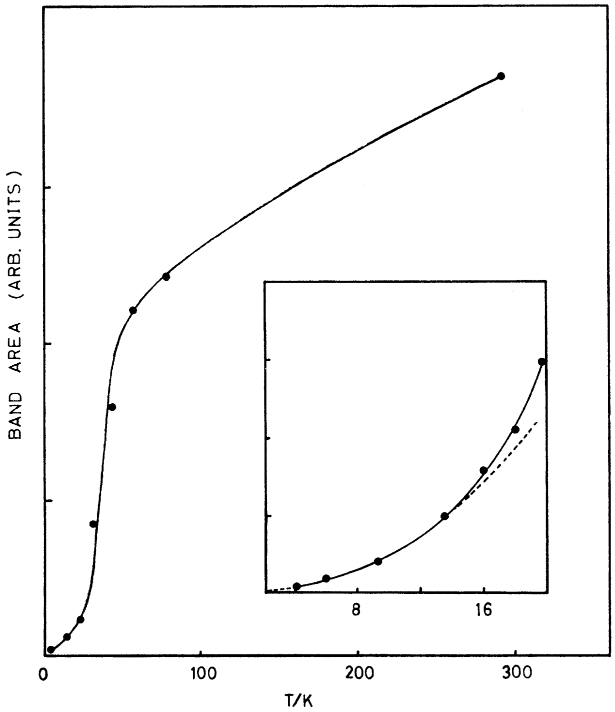

FIG. 2. Temperature variation of the intensity of the intensity of the 15 900 cm^{-1} transition in K_2CrCl_4. The inset shows the detailed intensity variation from 4.2 to 20°K. The dashed line is $f = aT^2$.

strength below 20°K is quite well approximated as T^2, drawn as the dashed line, normalized to 4.2°K, and to 0°K on the assumption that the oscillator strength is then zero. The temperature variation of the 18 700-cm^{-1} band is somewhat similar, though there are differences in the detailed behavior below 65°K.

From the d^4 Tanabe-Sugano diagram[12] it is clear that any transitions in this spectrum between 14 000 and 25 000 cm^{-1} are of triplet parentage. A phonon-assisted mechanism for the dipole strength of the 15 900- and 18 700-cm^{-1} bands is ruled out by the unusual form of their temperature dependence, which bears no resemblance to a hyperbolic-cotangent function. On the other hand, second-order spin-orbit mixing with the components of $^5T_{2g}$ would not account for the unusually high intensity of the two lines. In fact, it appears qualitatively that their intensity is related to the magnetization. In antiferromagnets such as $\mathrm{KNiF_3}$ the intensities of spin-forbidden ligand-field transitions follow the sublattice magnetization $M(T)$ quite closely, and depend on short-range order above T_N.[13] In the present ferromagnetic example a more appropriate function, at least as a first approximation, would appear to be $1-M(T)/M(0)$. Short-range order above T_c, and the contribution of vibronic intensity, could account for the departure of the experimental curve (Fig. 2) from this simple function. We believe, therefore, that the main contribution to the intensity of our two lines is an exchange-induced electric dipole mechanism. Since all the lines so far observed in the 14 000–20 000-cm^{-1} region have similar temperature dependence, it seems likely that they are all exciton-magnon combinations and that with the equipment used to record the spectra in Fig. 1 (Cary type 14 spectrometer), the pure exciton lines remain undetected.

In contrast to the situation in antiferromagnets, which have been very widely studied, in ferromagnets only "hot-band"[14] exciton-magnon absorption is possible. Either creation of an exciton is accompanied by annihilation of a thermally created magnon or the electronic excitation takes place from a thermally populated magnon state. Indeed, the temperature variation of the oscillator strength in Fig. 2 is remarkably similar to that calculated by Shinagawa and Tanabe[14] for the "hot-band" contribution to the exciton-magnon electric dipole strength in an antiferromagnet. It is also worth noting that the energies of the sharp lines in $\mathrm{K_2CrCl_4}$ remain invariant up to 78°K, an observation which is also consistent with absorption by the "hot-band" mechanism.

Precise assignments of the ligand-field excited states responsible for the two narrow absorption bands in $\mathrm{K_2CrCl_4}$ are difficult to decide because of the density of triplet levels in the relevant region of the Tanabe-Sugano diagram. In O_h symmetry these are $^3T_{1g}$, ^3E_g, $^3T_{1g}$, and $^3T_{2g}$ from ^3H, $^3A_{2g}(a^3F)$, and $^3A_{1g}(^3G)$. However, surveying known examples of d^4 ligand-field spectra, we find that in those compounds in which magnetic interactions, ferromagnetic or antiferromagnetic, are present [i.e., various binary and ternary Cr(II) fluorides[15,16] and chlorides,[4] $\mathrm{CrI_2}$[17] and $\mathrm{MnF_3}$[18]], two relatively intense spin-forbidden transitions are always observed, between 15 000 and 20 000 cm^{-1} in the Cr(II) compounds, and at 19 100 and 23 200 cm^{-1} in $\mathrm{MnF_3}$. To aid the assignment we have diagonalized the d^4 ligand-field matrices with and without the assumption of tetragonal symmetry and including spin-orbit coupling. We find that with the assumption that the two intense bands result from analogous transitions in each case, their positions are well represented simply by the nephelauxetic variation of the Racah parameters B and C even though the compounds surveyed represent a wide variety of metal-ion site symmetries. This implies either (i) the ligand-field states retain their cubic symmetry, or (ii) the lower than cubic symmetry states are insensitive to distortions in the ligand field. For (i) the assignment would be $^5E_g \rightarrow {}^3E_g(^3H)$ and $^5E_g \rightarrow {}^3A_{1g}(^3G)$. If (ii) applied, and with the assumption that the sign of the tetragoal distortion is such that the $^5B_{1g}$ component of the $^5E_g(O_h)$ ground state lies lowest, the two tetragonal components of the excited O_h triplet states listed above would be $^3B_{1g}$ of $^3E_g(^3H)$ and $^3B_{1g}$ of $^3A_{2g}(a^3F)$.

Further detailed investigations on $\mathrm{K_2CrCl_4}$ and other members of the $M_2\mathrm{Cr}X_4$ series are in progress, and will be reported in due course.

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Thermopower Anomaly in $GdNi_2$: Spin Scattering Model Versus Static Entropy Model*

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The thermopower anomaly in the vicinity of the ferromagnetic critical point of $GdNi_2$ has been measured and found to be of the form predicted by the spin disorder scattering model proposed recently by Thomas, Levin, and Parks. These results allow a vivid comparison between the above model and the idea that the anomalous thermopower measures the static electron entropy in metals, which has been recently discussed by Tang, Kitchens, and Craig.

In a recent Letter the critical thermopower of a metal in the vicinity of a second-order phase transition was worked out.[1] The basic approach was to take the formula for the thermopower derived by Mott and Jones,[2] $Q \propto |d\rho/d\epsilon|_{\epsilon_F}/\rho$, and assume that the critical portion of the resistivity ρ can be described by the Born scattering of the conduction electrons from localized critical fluctuations. The final result may be written in the form

$$\rho Q/T = A\rho_n + B\rho_c + C\Gamma(2k_F, T), \tag{1}$$

where ρ_n is the normal resistivity, ρ_c is the critical resistivity given by

$$\rho_c \propto k_F^{-4} \int_0^{2k_F} \Gamma(k, T) k^3 \, dk, \tag{2}$$

$\Gamma(k, T)$ is the spin-spin correlation function, and A, B, and C are constants. Results were presented in Ref. 1 for the critical thermopower anomaly in β-brass. While the results appeared to be more compatible with the above analysis than the static entropy model,[3-5] which predicts a strict correspondence between the thermopower anomaly and the specific heat anomaly, data scatter due to the smallness of the anomaly precluded distinguishing between Eq. (1) and the less precise result,

$$\rho Q/T = A\rho_n + D\rho_c. \tag{3}$$

Note from Eq. (2) that $\Gamma(2k_F, T)$ and ρ_c are roughly similar.

Previous studies of $GdNi_2$ have revealed that it behaves in a unique manner, in that mean-field behavior appears to hold unusually close to T_c, which turn implies an unusually long spin-spin force range. This is manifested in the magnetic susceptibility as a decrease in the value of the critical exponent γ with inceasing temperature close to and above T_c,[6,7] and in the electrical resistivity as a dramatic change in the slope of $d\rho/dT$ close to and above T_c.[8,9] Because of the latter feature, $GdNi_2$ is a particularly appropriate system in which to test the two models discussed above, since the predictions of the two models are strikingly different.

The $GdNi_2$ sample used in the experiment was prepared by arc melting 99.99% Gd and 99.95% Ni in an argon atmosphere. The sample was annealed for 24 h at 1000°K, then cut into a rectangular shape, 16mm × 2mm × 3mm, suitable for the thermoelectric power (TEP) measurements. Typical values of the temperature difference used