

FIG. 3. Microwave power at 9300 Mc/sec (A) and 24850 Mc/sec (B) produces many zero-slope regions spaced at $h\nu/2e$ or $h\nu/e$. For A, $h\nu/e = 38.5 \mu\text{V}$, and for B, $103 \mu\text{V}$. For A, vertical scale is $58.8 \mu\text{V/cm}$, horizontal scale is 67 nA/cm ; for B, vertical scale is $50 \mu\text{V/cm}$, horizontal scale is $50 \mu\text{A/cm}$.

pears to be a negative resistance at the origin. Negative-resistance-like regions occur between virtually every pair of zero-slope regions. At power levels of about ten milliwatts, these negative-resistance-like regions gradually vanish (the sample can be biased to any voltage), and the "zero-slope" regions exhibit a finite slope. Both these high-power effects are probably due to the superimposed conventional detection processes associated with the background single-particle tunneling curve.

3. Similar effects occur at 24 000 Mc/sec.

Figure 3 shows the numerous steps at 9300 Mc/sec (A) and at 24 850 Mc/sec (B) which are present at intermediate microwave power levels.

Josephson¹ has already discussed briefly the effect rf should have on the pair-tunneling supercurrent. He predicted the occurrence of zero-slope regions separated by $h\nu/2e$ in the I - V characteristic in the presence of the rf field. This prediction was based on the frequency modulation by the rf of the ac supercurrents previously referred to. Our experiments have confirmed this prediction and represent indirect proof of the reality of Josephson's ac supercurrent. In addition, they have brought to light several startling accompaniments of the Josephson effect, namely, the instability of the origin; the dc negative resistance at the origin; the noise associated with the onset of instability; and the periodic change at a given voltage level, e.g., at zero voltage, between stable and unstable as the microwave power changes.

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ANOMALOUS SHIFTS IN THE FLUORESCENCE OF MnF_2 AND KMnF_3

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In this Letter measurements are reported of large temperature-dependent changes in the fluorescence of MnF_2 and KMnF_3 . These changes take the form of relatively abrupt alterations in the wavelength and intensity of the fluorescence. The effects appear to be related to exchange interactions. To our knowledge, they have not been observed or reported previously.¹ We have observed similar effects in KMnCl_3 ,² but these effects were absent in the luminescence of $\text{K}(\text{Mn}_{0.01}\text{-Zn}_{0.99})\text{F}_3$ ³ and MnCl_2 .⁴

The fluoride crystals used in these experiments

were grown by the horizontal Bridgman technique and the temperature gradient method in an HF atmosphere. The observations were performed using a Perkin-Elmer Model 12-C spectrometer. The crystals were mounted on a copper post in a metal Dewar provided with windows for optical access. Separate thermocouples monitored the temperature of both the post and the sample attached to the post.

The procedure for taking measurements began with the cooling of the sample by placing liquid helium in the coolant reservoir of the Dewar. Af-

ter the coolant had boiled away, the temperatures of the post and the attached sample would rise. The thermal mass of the system provided a sufficiently slow rate of warming for these measurements. During the warming period, profiles of the spectra and temperature measurements were simultaneously recorded. The post and sample temperatures differed from one another by less than 4°K , the largest difference occurring at the lowest temperatures. The accuracy of the measurements of the fluorescence peak was estimated to be 20 \AA at the lower temperatures. The inaccuracy became somewhat larger at higher temperatures because of the interference of the excitation source background and the deterioration of the signal-to-noise ratio.

The fluorescence of MnF_2 could be excited by monochromatic radiation in any of the five lowest lying absorption lines of the Mn^{2+} ion.⁵ For convenience, the 4358 \AA blue line of a mercury arc [corresponding to the ${}^4T_{2g}({}^4G)$ level] was used during the experiments. Because of weaker fluorescence intensity, a commercial uv lamp excitation source was used for KMnF_3 and $\text{K}(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{F}_3$.

In Fig. 1, the detailed behavior of the wave-

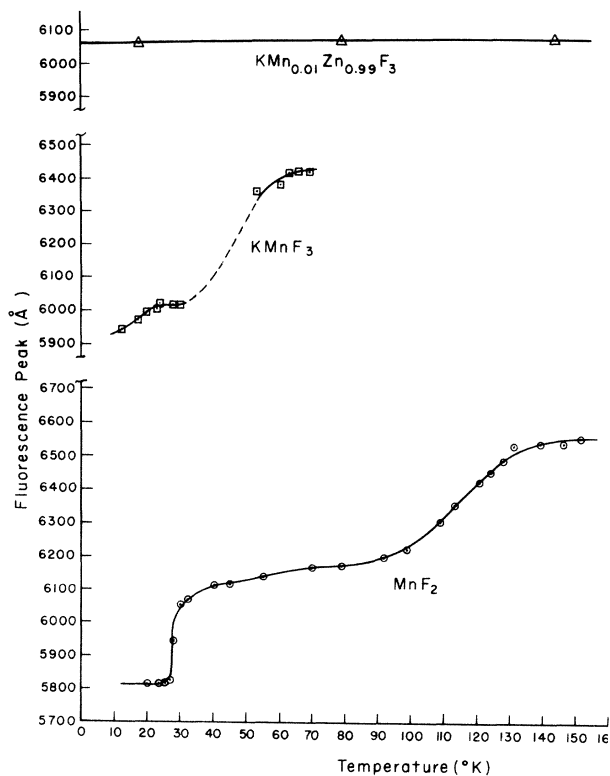


FIG. 1. Temperature dependence of the fluorescence maxima of MnF_2 , KMnF_3 , and $\text{K}(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{F}_3$.

length of the fluorescence maxima is presented for the three fluoride crystals. The line shape was substantially independent of temperature. The width of the MnF_2 fluorescence (as measured at half-height) was approximately 500 \AA at 22°K , and approximately 650 \AA at 65°K . In this same temperature range the width of the $\text{K}(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{F}_3$ fluorescence was nearly constant at 530 \AA , while in less accurate data the linewidth of KMnF_3 appeared to broaden from 500 \AA to 580 \AA . A feature of Fig. 1 which is particularly interesting is that for MnF_2 the alteration of the fluorescence wavelength is not uniform but occurs in two moderately abrupt "jumps." The magnitude of each "jump" is roughly the same and relatively large (about 370 \AA). To the eye the transformation is quite striking as the low temperature fluorescence changes from a bright yellow to orange to a weak red color as the temperature is increased. As implied in this description, there is an associated temperature dependent variation in the intensity. This is shown in Fig. 2.

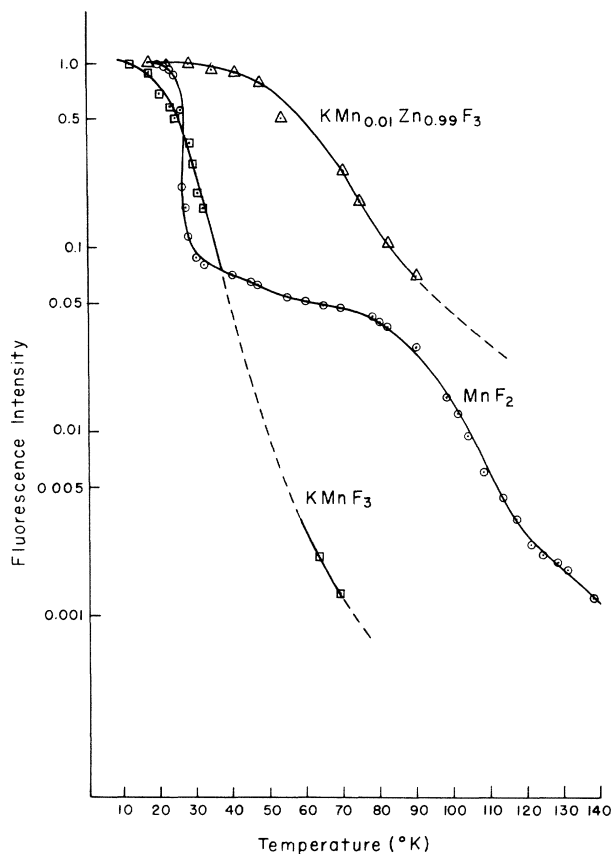


FIG. 2. Temperature dependence of the intensity of the fluorescence of MnF_2 , KMnF_3 , and $\text{K}(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{F}_3$, each normalized with respect to maximum value.

As shown in Figs. 1 and 2, KMnF_3 showed an effect quite similar to MnF_2 . However, because of the weaker fluorescence, it could be measured only over a narrower temperature region. There was no observable shift in the fluorescence of $\text{K}(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{F}_3$, and its intensity followed expected behavior. It is noted in passing that KMnCl_3 ² but not MnCl_2 showed a similar striking change in fluorescence at low temperatures.

Orgel⁶ has interpreted the fluorescence spectra of dilute manganese systems as a transition from the ${}^4T_{1g}({}^4G)$ excited state to the ground state in a lattice site which has been changed from its normal configuration. The lattice distortion arises from the altered manganese-anion interaction energy of the excited state. This model⁷ is adequate to explain the temperature independence of the Stokes shift relative to the corresponding absorption transition and the breadth of the fluorescence line of such dilute systems as the $\text{K}(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{F}_3$. However, it does not appear adequate to explain our results with pure manganese compounds.

Both MnF_2 and KMnF_3 undergo transitions to the ordered antiferromagnetic state at relatively high temperatures [$T_N(\text{MnF}_2) = 67^\circ\text{K}$, $T_N(\text{KMnF}_3) = 88^\circ\text{K}$]. This indicates a strong exchange interaction between the manganese ions. It may be expected that this interaction would be in some way reflected in the fluorescence spectra. The comparison of the behavior of the isostructural KMnF_3 and $\text{K}(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{F}_3$ crystals shows clear evidence for such interaction effects. In the dilute $\text{K}(\text{Mn}_{0.01}\text{Zn}_{0.99})\text{F}_3$ crystal, the fluorescence wavelength was substantially independent of temperature and the fluorescent yield very nearly constant below 50°K . In contrast, both the KMnF_3 and the MnF_2 show their most pronounced effects in both wavelength and yield below this temperature.

The energy shifts observed in the fluorescence spectra ($\sim 10^3\text{ cm}^{-1}$) are large compared to the antiferromagnetic energies ($\sim 50\text{ cm}^{-1}$). It does not therefore seem reasonable that exchange splitting effects are directly responsible for the observed phenomena. We suggest that magnetic ordering provides an additional source of local lattice distortion around the excited ion which in turn gives rise to the effects described.

It has been pointed out that bond strengths and energies are largely determined by σ bonding which mixes the e_σ and p_σ states of the transition metal and fluoride ion, respectively.⁸ The excited fluorescent state is $(t_{2g})^4e_g$. Thus, it might be expected that the reduced number of e_g orbitals in the excited state would result in a lattice dilation. Correspondingly, the number of unpaired t_{2g} and e_g orbitals is also reduced in the excited state. Therefore, one would expect the antiferromagnetic exchange energy between the excited ion and its neighbors to be reduced accordingly. Thus, at very low temperatures where the excited state is antiferromagnetically aligned, one would expect the lattice dilation effect to be partially canceled by the lattice contraction due to the antiferromagnetic exchange coupling. At some higher temperature, less than the Néel temperature, thermal energy will be sufficient to disorient the excited-state spins and this cancellation would not occur. We believe that the very abrupt decrease in the fluorescence wavelength at temperatures above 20°K , for both MnF_2 and KMnF_3 , can be understood in this way.

We point out that in the 70°K to 120°K range, where the second shift in the MnF_2 fluorescence is observed, changes in the a axis have been reported.⁹ This would alter the ground-state configuration, modifying the fluorescent wavelength.

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²This is the tentative identification of this phase.

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