density of liquid and saturated vapor of lead are

	T, °K.	$D_{\text{liq}^{3}}$, g./cm.^{3}	$D_{\text{id. gas}}$, g./cm.^{3}
Experimental values	1600	9.361	. . .
	2024 (N.B.P.)	8.803	0.0012
Extrapolated values	2500	8.167	0.008
	3000	7.49	0.029
	3500	6.79	0.072

If Gates and Thodos' value of 3584°K. for T_c of Pb is correct, there should be a sudden change in the whole density *vs.* temperature relationship for the liquid and saturated vapor beyond the normal boiling point, in contrast to all known liquids.

The knowledge of true critical temperatures permits us to establish a very simple density *vs.* temperature relationship[1-3] for most of the liquid range of any metal and also the change in surface tension or energy *vs.* temperature for any metal.[16]

It goes without saying that it would be highly desirable to determine the critical temperature of other metals besides mercury; some of them are certainly within reach of modern high temperature experimentation.

[16] A. V. Grosse, *J. Inorg. & Nuclear Chem.*, in press.

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Observation of Four d-d Transitions in a Copper Chelate[1]

Sir:

We have discovered four optical transitions, in the d-d absorption region, in single crystals of bis-(3-phenylacetylacetonato)-copper

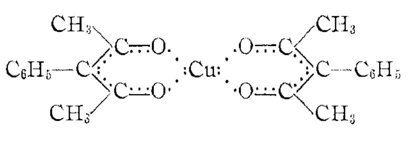

Fig. 1 and 2 show the spectra of a thin section of one face at room temperature and at liquid nitrogen temperature.

In view of the current diversity of opinion[2-5] concerning the assignments of the bands in the spectrum of the related compound, bis-(acetylacetonato)-copper, we think it worthwhile to show these preliminary results without the full analysis (which, including the necessity for a full X-ray structural determination and for observing other faces, will take us over a year to complete).

It is noteworthy that in addition to the four bands of comparable intensity in the visible, there is a stronger fifth band at slightly higher energy. This fifth band we have ascribed to a ligand transi-

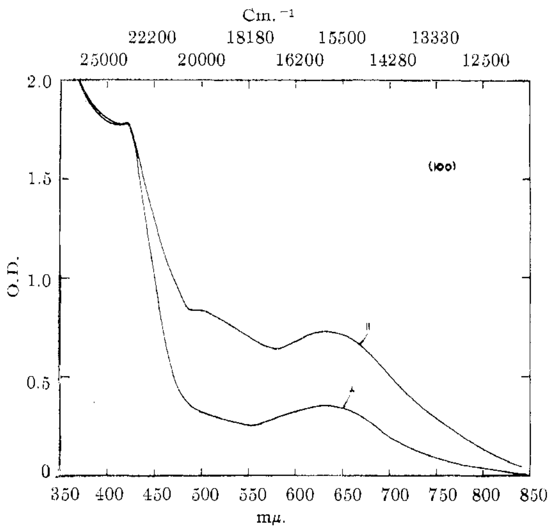

Fig. 1.—Polarized spectra of copper bis-3-phenylacetylacetonate (room temperature).

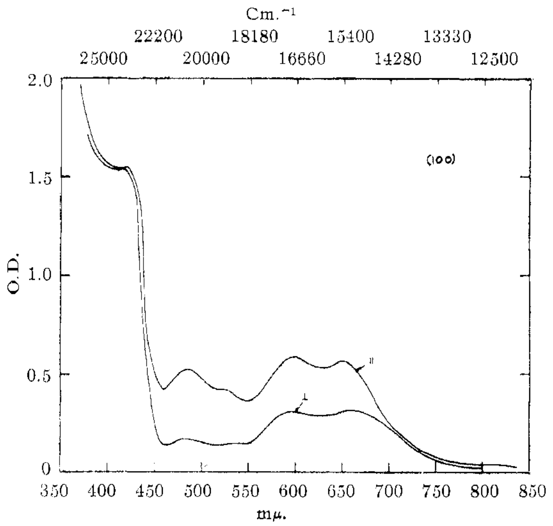

Fig. 2.—Polarized spectra of copper bis-3-phenylacetylacetonate (liquid nitrogen temperature).

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[1] This work is supported by the National Science Foundation and by an Alfred P. Sloan Foundation Research Fellowship awarded to R. L. Belford.

[2] T. S. Piper and R. L. Belford, *Mol. Phys.*, **5** (1962); R. L. Belford and T. S. Piper, *ibid.*, **5** (1962), both in press.

[3] J. Ferguson, *J. Chem. Phys.*, **34**, 609 (1961).

[4] D. P. Graddon, *J. Inorg. & Nuclear Chem.*, **14**, 161 (1960).

[5] R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

tion[2,5] but others have called it a d-d transition.[3,4,6] We suggest that the four visible bands are the four transitions crudely described as (xz ← xy), (yz ← xy), (x^2-y^2 ← xy), and ($3z^2$-r^2 ← xy) and that the fifth band must, therefore, be a ligand transition.

On the other hand there is a distinct possibility that the two lowest-frequency humps shown in Fig. 2 are the same electronic transition differing by a strongly-coupled carbonyl vibrational quantum in the upper state. (See, for example, the spectrum of tris-(acetylacetonato)-titanium.[7])

The possibility that the multiple spectral bands actually are caused by two copper atoms at non-equivalent sites has been considered. This is ruled out by an X-ray analysis of the crystal showing that there are two molecules per unit cell in chemically identical sites. The cell is monoclinic, $P2_1/C$ (a = 10.21 Å., b = 6.79 Å., c = 13.72 Å.; β = 93.8°).

The immediate environment of the Cu ion probably can be adequately described by C_{2v} or D_{2h} symmetry; splitting of the d antibonding levels into five components would be indicated. If the four predicted absorption bands are to be resolved, the ligands must be just right for the required splitting. Also, most copper chelate spectra previously reported were studied only at room temperature, where some of the bands broaden and merge. Therefore, the four transitions have not heretofore been separated clearly.

We particularly welcome communication from other workers who can suggest alternate interpretations, especially if they also can suggest ways that we can test the interpretations before we have finished experimenting on this problem.

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(6) A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958).

(7) R. L. Carlin and T. S. Piper, unpublished but shown in the Ph.D. thesis of R. L. Carlin, University of Illinois, 1960.